RHEOLOGY OF POLYMER NANOCOMPOSITES FOR ADVANCED TIRE TREAD COMPOUNDS

Undergraduate Research Thesis

Presented in partial fulfillment of the requirements for Graduation with Honors Research Distinction in the College of Engineering of The Ohio State University

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ABSTRACT

The primary objective of this research was to explore polymer and nanoparticle interactions that effect rheological properties related to increasing grip while decreasing rolling resistance in tires. Generally, grip generates far greater forces than rolling resistance. With the addition of nanocomposites such as silica, however, the material can store more energy at low frequencies and dissipate more energy at higher frequencies. This results in lower rolling resistance while maintaining strong grip. The material that was used is polystyrene and polybutadiene, less complex polymers that are easier to model compared to the commonly used styrene-butadiene rubber (SBR). The nanocomposite that was added to the polymer is silica, which ranges from 5-50 nm and is coated in silane coupling agent. The nanocomposite material was tested with frequencies from 10^{-1} to 10^{3} Hz and at 200°C. The viscosity, storage and loss modulus, and dissipating factor (tan delta) was calculated using a dynamic frequency sweep test. The results showed that the addition of silica to polystyrene significantly increases the storage modulus of the material at low frequencies, improving rolling resistance. Minimal increases in loss modulus at high frequencies related to grip were noticed. Inconclusive data was found when adding silica to polybutadiene. The results using polystyrene can be utilized as a model for understanding nanoparticle interactions in other complex materials.

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Kurt Koelling, for the opportunity to work on this project, his instruction, and his encouragement in finishing the research that seemed daunting at times. I would also like to thank Varun Venoor for his continued guidance and his contribution to much of the data collection. I sincerely appreciate Dr. Lisa Hall, Alex Trazkovich, and other students in the research group that have taught me more about rheology and added new suggestions and ideas. Thank you to Cooper Rubber & Tire Company for providing materials and information about tires.

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INTRODUCTION

Today, it is common for most Americans to own a vehicle for convenient travel. More than 250 million tires were sold in the United States in 2014 and consumers spent almost 40 billion dollars [1]. Understanding how to improve the tire is crucial in improving overall safety, maneuverability, and efficiency of the vehicle [2]. With greater distances to cover and an emphasis on safety and efficiency, the material of the tire must be carefully examined in order to produce the best product. The primary objective of this research is to explore polymer and nanoparticle interactions that effect rheological properties related to increasing grip while decreasing rolling resistance in tires.

For tires, the most important properties to consider are grip and rolling resistance. Without grip, cars would not be able to move at all. Grip is essential when considering directional stability and safety. The ability for vehicles to brake quickly even in wet conditions could mean the difference between a gentle bump and a fatal accident. Safety is a necessity for any tire company. Rolling resistance is the energy required to keep the tires rolling at a straight and steady pace. Having a lower rolling resistance means that less fuel is required to keep the car running at a steady pace. Fuel efficiency is a major selling point to consumers because oil prices are constantly on the rise. With a 10% reduction in rolling resistance, fuel efficiency improves by approximately 1.5%. In 2009, the National Highway Transportation and Safety Administration estimated that a 10% average rolling resistance reduction across all passenger and light truck tires in the United States would save US consumers more than one billion gallons of fuel per year [3]. In an effort to move away from carbon emissions, any potential energy saved from reducing rolling resistance is significant for new electric vehicles to travel farther distances without oil. Unfortunately, it is difficult to improve both grip and reduce rolling resistance. For

typical rubbers, when grip increases, rolling resistance is also increased. Ideally, grip should be increased while rolling resistance is decreased so that the tire can offer all benefits to consumers.

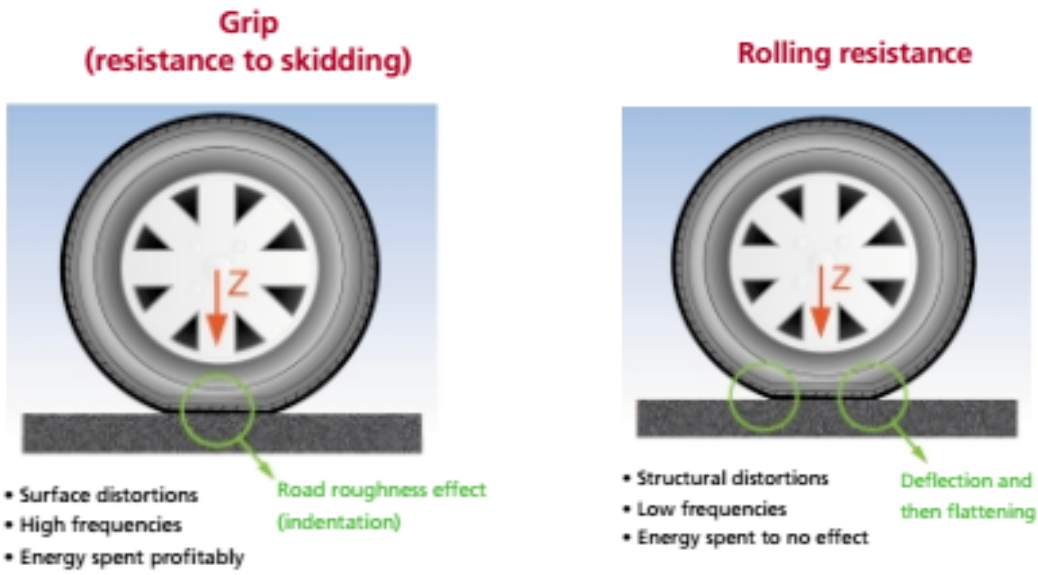

Figure 1: Comparison of grip and rolling resistance in tires [2]

As seen in Figure 1 above, grip corresponds to the deformation of the tire's surface while rolling resistance is related to the deformation of the structure as a whole. The tire's tread blocks wrap around the rough spots in the road surface in order to generate grip and the weight of the car deforms the entire width and thickness of the tire resulting in energy loss. Energy loss is important for grip because the energy is spent profitably in gripping the road. Energy stored is important for rolling resistance because it is ideal to reduce as much energy loss as possible when that energy is spent to no effect.

In order to produce the best product, it is significant to understand the rheological properties that govern grip and rolling resistance. Tires are made primarily with rubber, a viscoelastic material. A viscoelastic material is a deformable material with a behavior which lies between that of a viscous liquid and an elastic solid. The rubbers of the tire are vulcanized elastomers that are made up of one or more polymers. Sulfur bridges between the polymer chains

fasten the chains so that it acts like an elastic spring. However, the friction between the molecules gives the material its viscous property. The viscoelasticity of rubber is most significant because of hysteresis, the delay in which the material reverts back to its initial shape after it has been deformed. This delay is accompanied by a loss of energy associated with rolling resistance. With an emphasis on grip, hysteresis must be increased. Hysteresis is maximum at a high frequency with which the force is applied. By increasing hysteresis and grip in the tire, a greater loss of energy is inevitably involved, increasing rolling resistance.

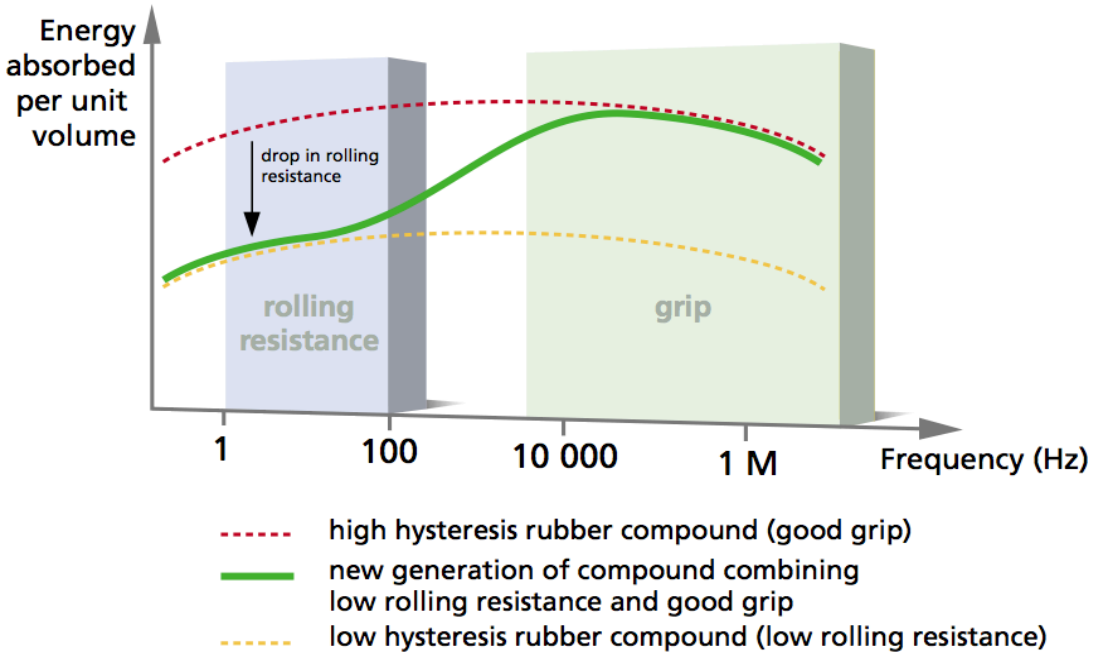

Figure 2: Energy absorption for ideal tire tread [2]

At first glance, it may appear impossible to reduce rolling resistance without compromising grip. However, grip generates far greater forces than rolling resistance. The distortion of the tire's surface that generates grip occurs at stress frequencies between 10^3 and 10^{10} Hz. However, the deformation of the structure occurs each time the wheel rotates, at approximately 15 Hz. Conclusively, grip and rolling resistance are related to different frequency

ranges. Rubber compounds will absorb similar amounts of energy at differing frequencies and result in a flat energy absorption curve. With the addition of nanocomposites such as carbon black and silica, however, the material can absorb less energy at lower frequencies and more energy at higher frequencies, as seen in Figure 2 above. This results in lower rolling resistance while maintaining strong grip.

MATERIALS AND METHODOLOGY

A. Description of Materials

Polystyrene and polybutadiene were the polymers studied and silica was the nanoparticle blended into the composite. Approximately 50% of tires are produced with SBR (styrene butadiene rubber) [4]. SBR describe synthetic rubbers derived from styrene and butadiene. The material has good abrasion resistance and good aging stability, which is ideal for tires. The styrene/butadiene ratio influences the properties of the polymer. The structure of the repeating unit can be found below in Figure 3.

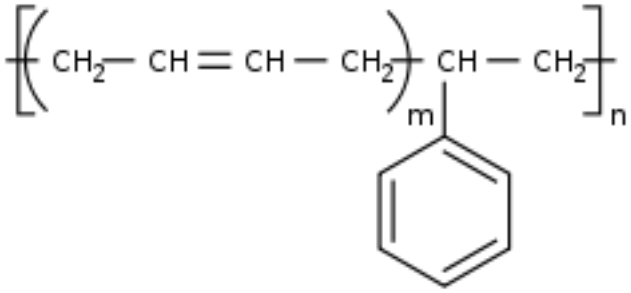

Figure 3: Structure of styrene butadiene rubber (SBR)

To understand the rheology of typical tire materials, which are composed of silica in crosslinked SBR along with various additives, simplified systems of silica nanoparticles dispersed in pure polystyrene and pure polybutadiene were studied.

Nanoparticle fillers such as carbon black and silica are a key component of tire tread compounds. Compared to carbon black, the use of silica as reinforcing filler for rubber results in lower hysteretic losses [5]. However, the surface chemistry of silica nanoparticles is significantly different from carbon black because of the existence of silanol groups [6]. The hydrophilic silica is incompatible with hydrophobic rubber polymer matrix. As a result, silica nanoparticles have the tendency to form large conglomerates instead of dispersing evenly into the polymer matrix.

Therefore, silane coupling agents, which are capable of reacting with the silica surface and the polymer will be applied in order to reduce the polarity difference. Silica ranges from 5-50 nm and is spherical in geometry.

The polystyrene used was received from Chevron Phillips Chemical Company LP (MC 3600, Specific gravity: 1.03, MFI: 13.0 g/ 10 min at 200ºC). Cooper Tire & Rubber Company provided the polybutadiene and silica pretreated with a silane coupling agent.

B. Experimental Methodology

To compound the polymer nanocomoposites, a DACA microcompounder was utilized to melt blend the polymer and nanoparticle. Polystyrene pellets and nanoparticles were weighed and then added to the compounder carefully throughout the top of the microcompounder. To ensure a more homogenous mixture, the polymer and nanoparticle was added in parts until all of the sample was used. It is likely that weight percentages are inaccurate due to the difficulty of adding polymer pellets and nanoparticle powder to the small opening of the microcompounder. The mixture was allowed to stir for approximately 5 minutes at a temperature of 200ºC and 250 RPM. The materials were then cut into small pellets and melt pressed at 200ºC at 3500 psi for 15 minutes in order to form a circular disc in a mold with a diameter of 25 mm.

The disc was then placed on a parallel plate (25 mm) rheometer (TA Instruments ARES) and a dynamic frequency sweep test was performed at a temperature of 200ºC in order to determine storage and loss modulus, viscosity, and tan delta. The test was performed with a .845 mm gap from .1 to 1000 Hz at a controlled strain of 5% to stay within the linear viscoelastic regime.

The oscillatory deformation produces an oscillatory stress response within the material. The response can be decomposed into two waves, in-phase with the deformation and 90º out-of-phase. The in-phase response is referred to as the elastic response and the out-of-phase response is referred to as the viscous response. The elastic response stores energy and is quantified by storage modulus while the viscous response dissipates energy and is quantified by loss modulus. The ratio of loss modulus to storage modulus is define as tan delta. The relationships between strain, strain amplitude, frequency of oscillation, stress, storage modulus, loss modulus, and tan delta can be seen in the Equations below.

$\gamma = \gamma o \sin(\omega t)$

$\tau = G'\gamma o \sin(\omega t) + G''\gamma o \cos(\omega t)$

$\tan(\delta) = G'' G'$

RESULTS AND DISCUSSION

A. Rheological Testing for Polystyrene and Silica Composites

Samples were tested on a parallel plate rheometer at 200ºC in order to determine the rheological properties of pure polystyrene above the glass transition temperature for comparison to composites.

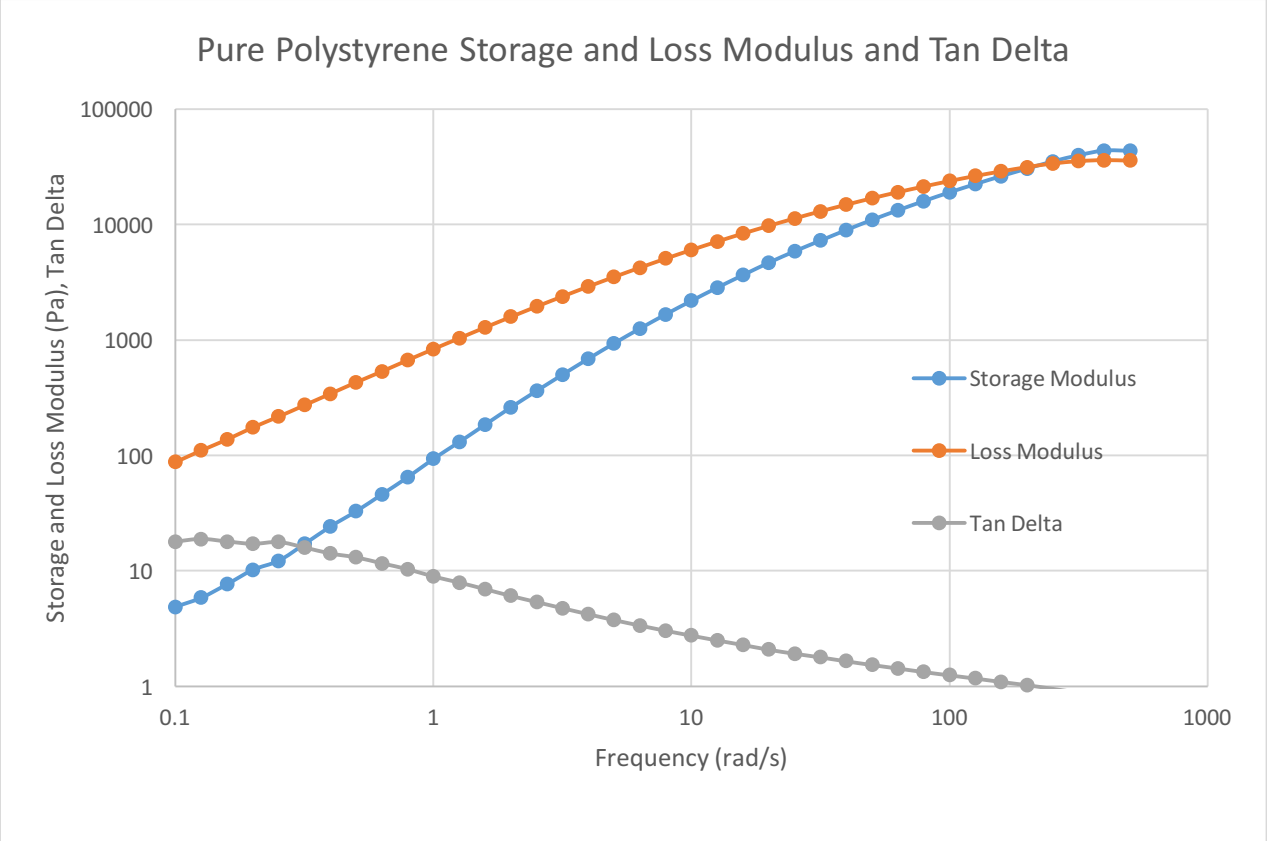

Figure 4: G' and G'' versus frequency for pure polystyrene

As seen in Figure 4 above, both the storage modulus and loss modulus increased as frequency increases. The storage modulus is the elastic solid behavior (G') and the loss modulus is the viscous response (G''). The curves cross when the frequency is equal to the reciprocal relaxation time. This is consistent with what is expected for viscoelastic fluids. As frequency or shear rate increased, the stress within the material also increased.

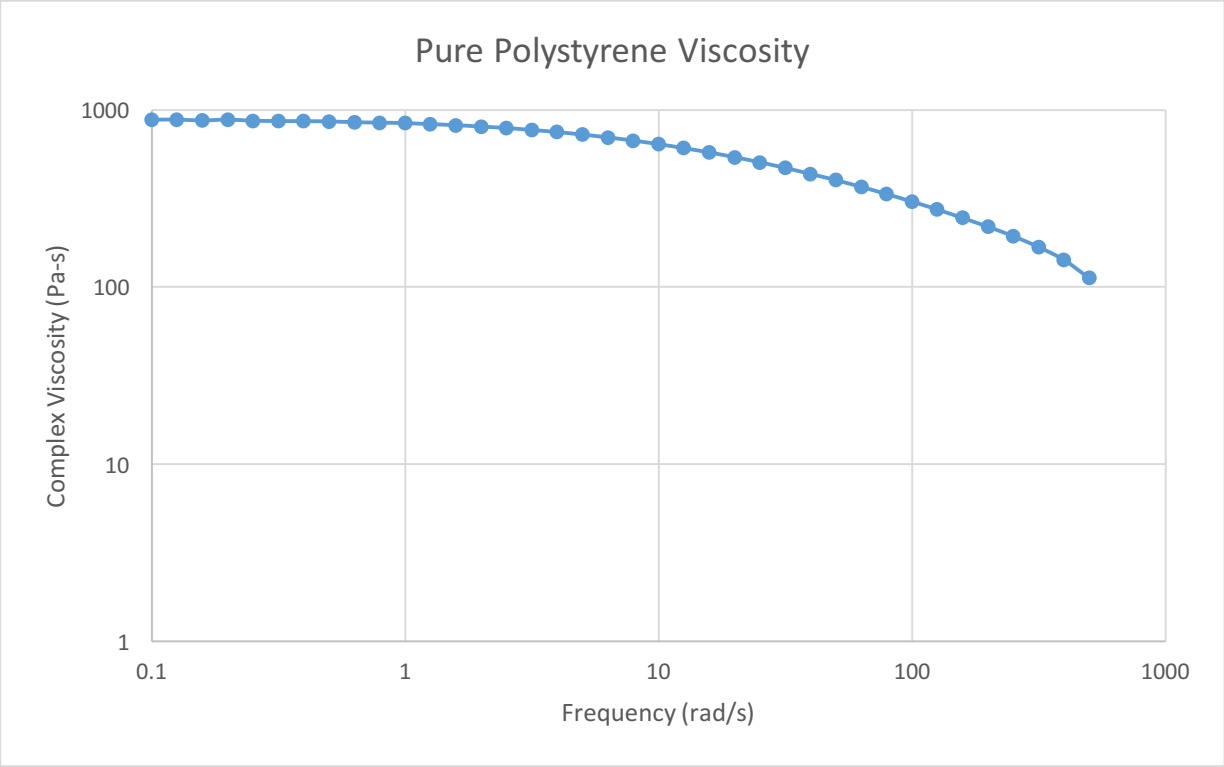

Figure 5: Complex viscosity versus frequency for pure polystyrene

As seen in Figure 5 above, the complex viscosity decreased with frequency. As frequency or shear rate increased, the viscosity decreased. This is consistent with shear thinning behavior in viscoelastic materials.

Silica particles were added to the polystyrene at varying weight percentages to improve the rheological properties desired. The results were compared to the pure polystyrene data. Three trials were performed for each weight percentage.

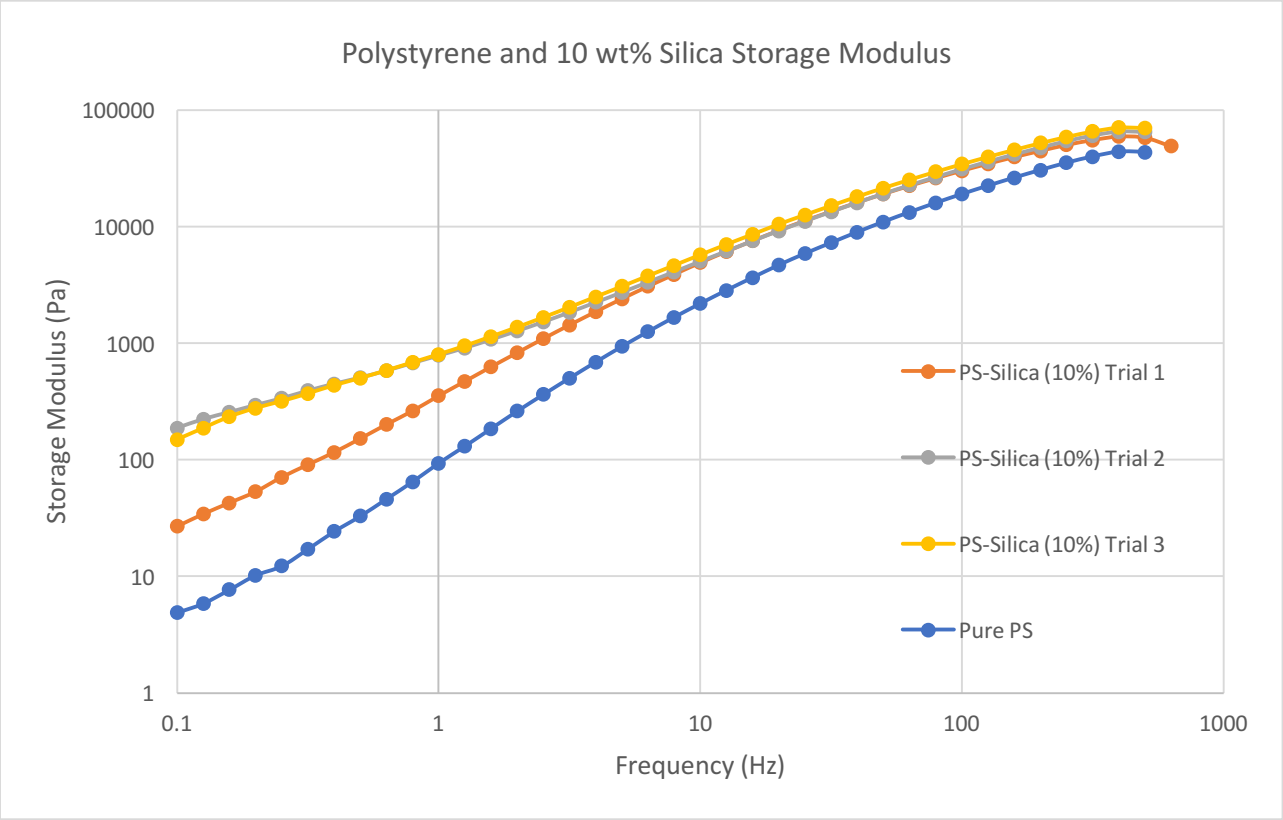

Figure 6: G' versus frequency for polystyrene and 10 wt% silica

As seen in Figure 6 above, the storage modulus increased at low frequencies for each trial in comparison to pure polystyrene. The storage moduli are similar at higher frequencies. Low frequencies are associated with rolling resistance. Rolling resistance is energy that is lost when the tire is rolling with constant deformation of the tire. As desired, the material's ability to return more stored energy reduces the rolling resistance in the tire. Varying weight percentages also exhibit similar trends and can be found in the Appendix.

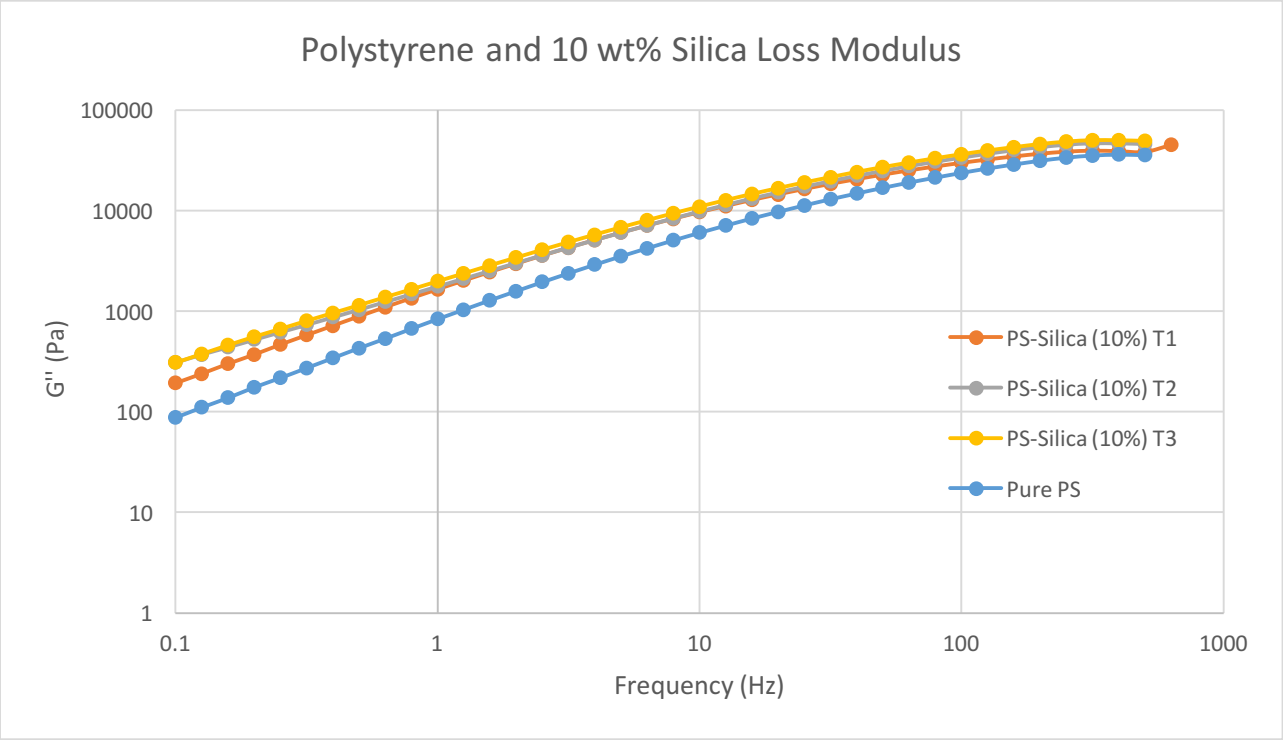

Figure 7: Loss modulus versus frequency for polystyrene and 10 wt% silica

As seen in Figure 7 above, the loss modulus increased at low frequencies for each trial in comparison to pure polystyrene. The loss moduli are similar at higher frequencies. High frequencies are associated with grip. Higher energy losses at higher frequencies improves the grip of the material. Unfortunately, the loss modulus at high frequencies is not significant different. Varying weight percentages also exhibit similar trends and can be found in the Appendix.

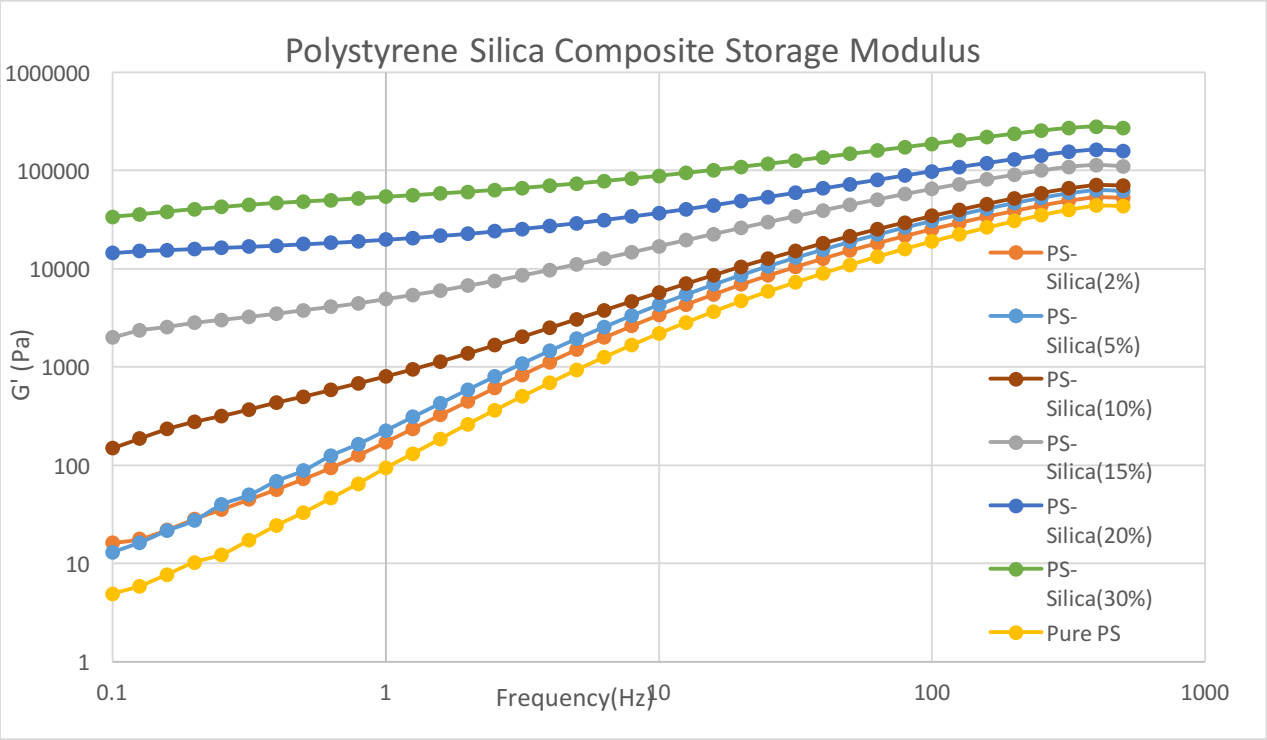

Figure 8: G' versus frequency for polystyrene silica composites at varying weight percentages

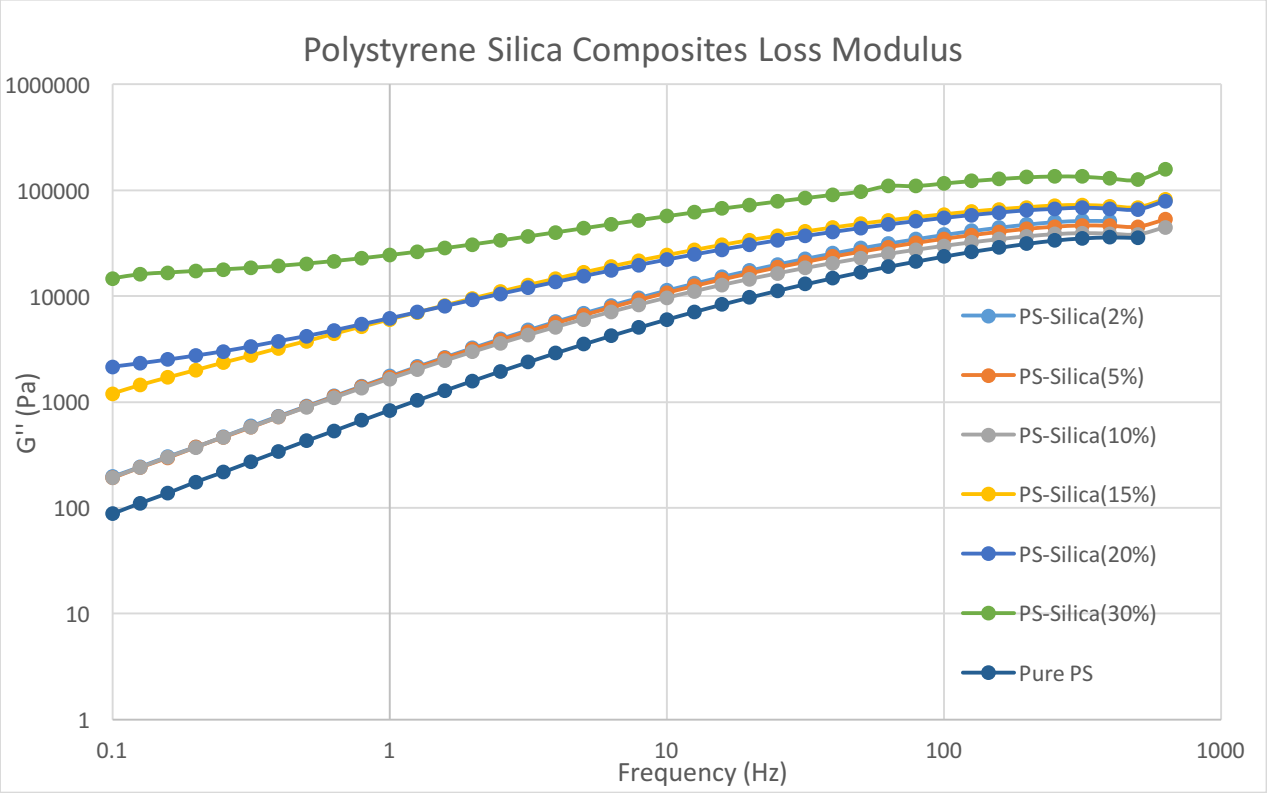

Figure 9: G'' versus frequency for polystyrene silica composites at varying weight percentages

As seen in Figure 8 and Figure 9 above, as silica weight percentage increases, the storage and loss modulus increased. The increases are greater at lower frequencies in comparison to higher frequencies. As desired, the material's ability to return more stored energy reduces rolling resistance in the tire. Because low frequencies are associated with rolling resistance, greater increases in storage modulus at low frequencies are preferred. However, at higher frequencies related to traction, an increase in storage modulus is not desired and losses of energy are needed instead.

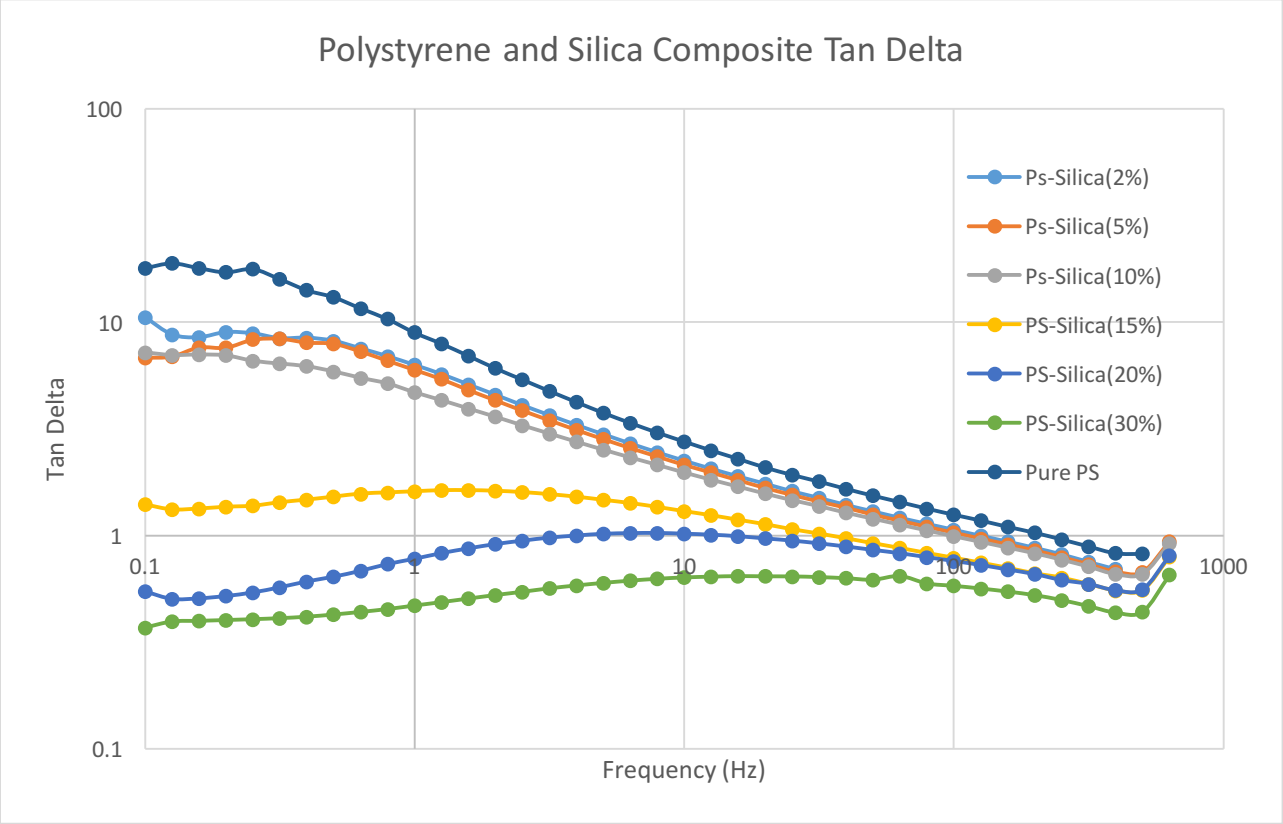

Figure 10: Tan Delta versus frequency for polystyrene and silica composites at varying weight percentages

As seen in Figure 10, the tan delta values are the ratio between loss modulus to storage modulus. At low frequencies, the tan delta value is desired to be low because energy stored reduces the rolling resistance. At high frequencies, the tan delta value is desired to be high

because energy lost increases grip. In the polystyrene silica composite, increasing the weight percentage of silica decreases the tan delta value dramatically at low frequencies. This successfully achieves reducing rolling resistance in the material. Unfortunately, the tan delta value decreases at high frequencies as well but not as significantly as the values at low frequencies. However, it is not desirable to compromise too much grip in order to improve rolling resistance.

B. Rheological Testing for Polystyrene and Silane Coated Silica Composites

Because silica particles are highly polar and likely to conglomerate within the composite, the silica particles were coated with silane before compounding to increase dispersion. The same tests as the polystyrene and silica composites were performed with silane coated silica particles.

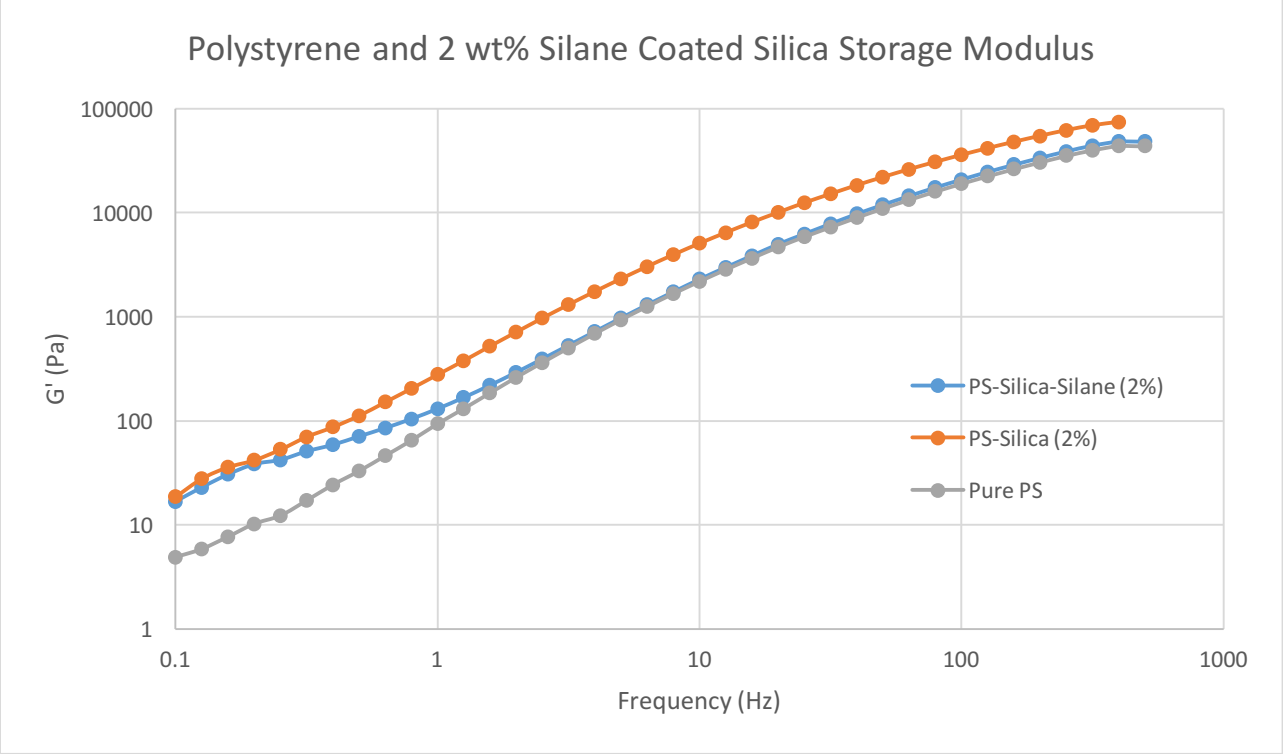

Figure 11: G' versus frequency for polystyrene and 2 wt% silica with and without silane

As seen in Figure 11 above, both composites show greater storage moduli at lower frequencies and similar storage moduli at higher frequencies. This is consistent with the results found previously. However, the composite with silane coated silica particles have a lower storage modulus in comparison to the composite with silica. No significant difference was noticed in adding silane and in fact, the silane had a negative effect on the storage modulus. Varying weight percentages also exhibit similar trends and can be found in the Appendix.

It was possible that the silane is improving dispersion of the silica particles but plasticizing the polystyrene. Thus, silane (without silica) and polystyrene was tested under the same conditions.

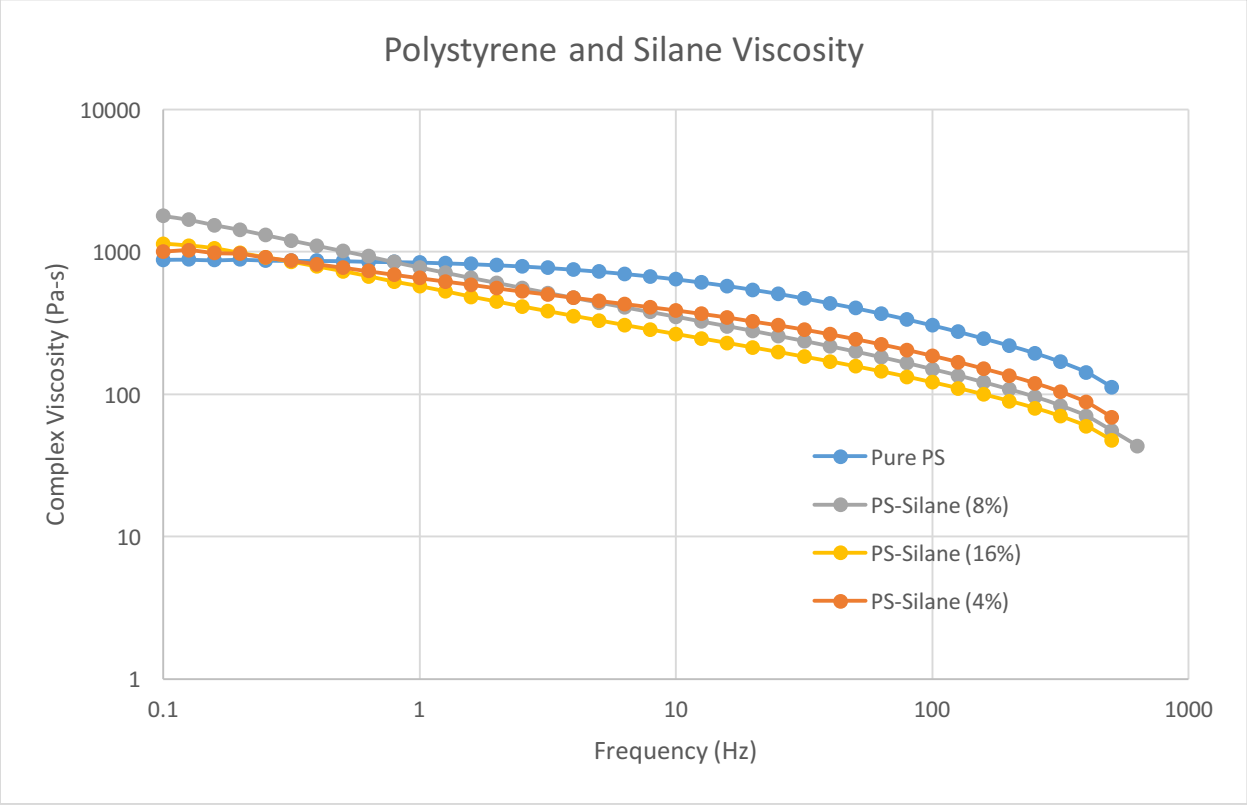

Figure 12: Viscosity versus frequency for polystyrene and silane

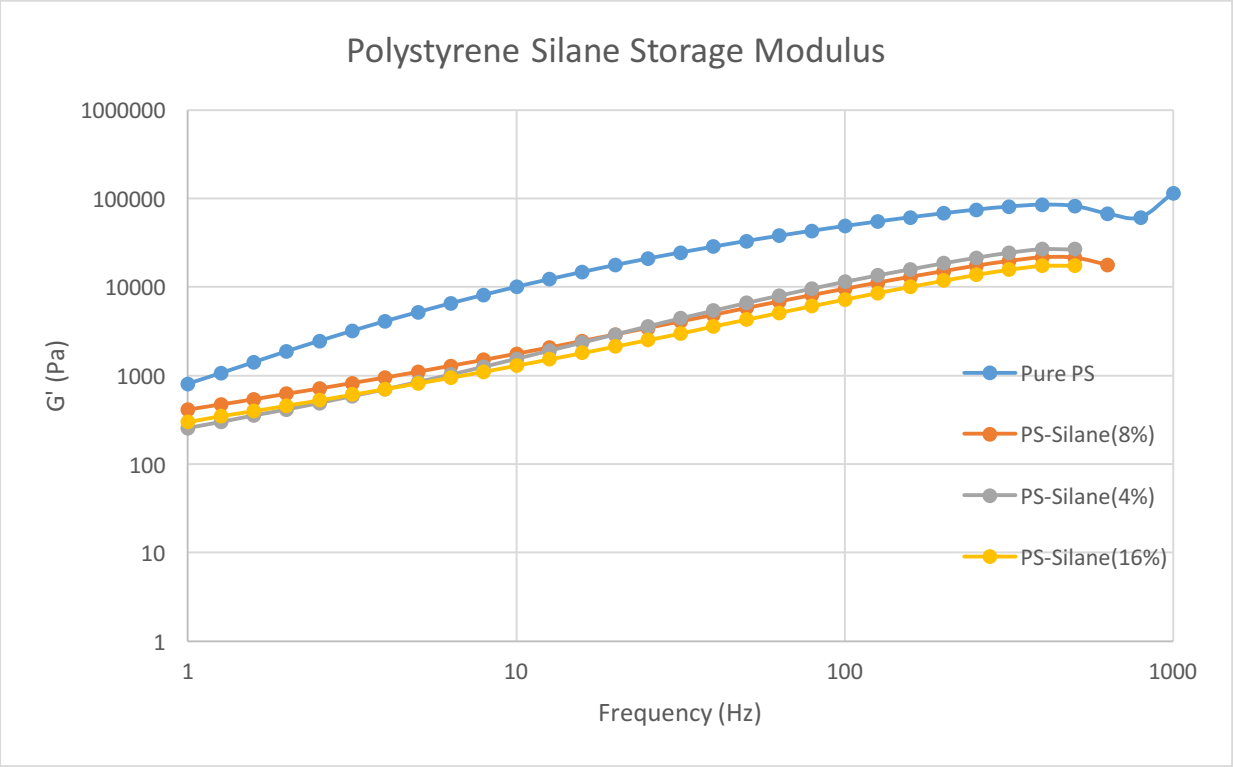

Figure 13: Storage modulus versus frequency for polystyrene and silane

As seen in Figure 12 and 13 above, the silane decreases the viscosity and storage modulus of the polystyrene. Thus, any increase in storage and loss modulus and viscosity gained by better dispersion is negated by the negative interactions between polystyrene and silane. It is likely that the silane was acting as a plasticizer within the polystyrene. In order to attempt to mitigate this error, the silane coated silica particles were treated with benzene to wash some of the silane off of the particles.

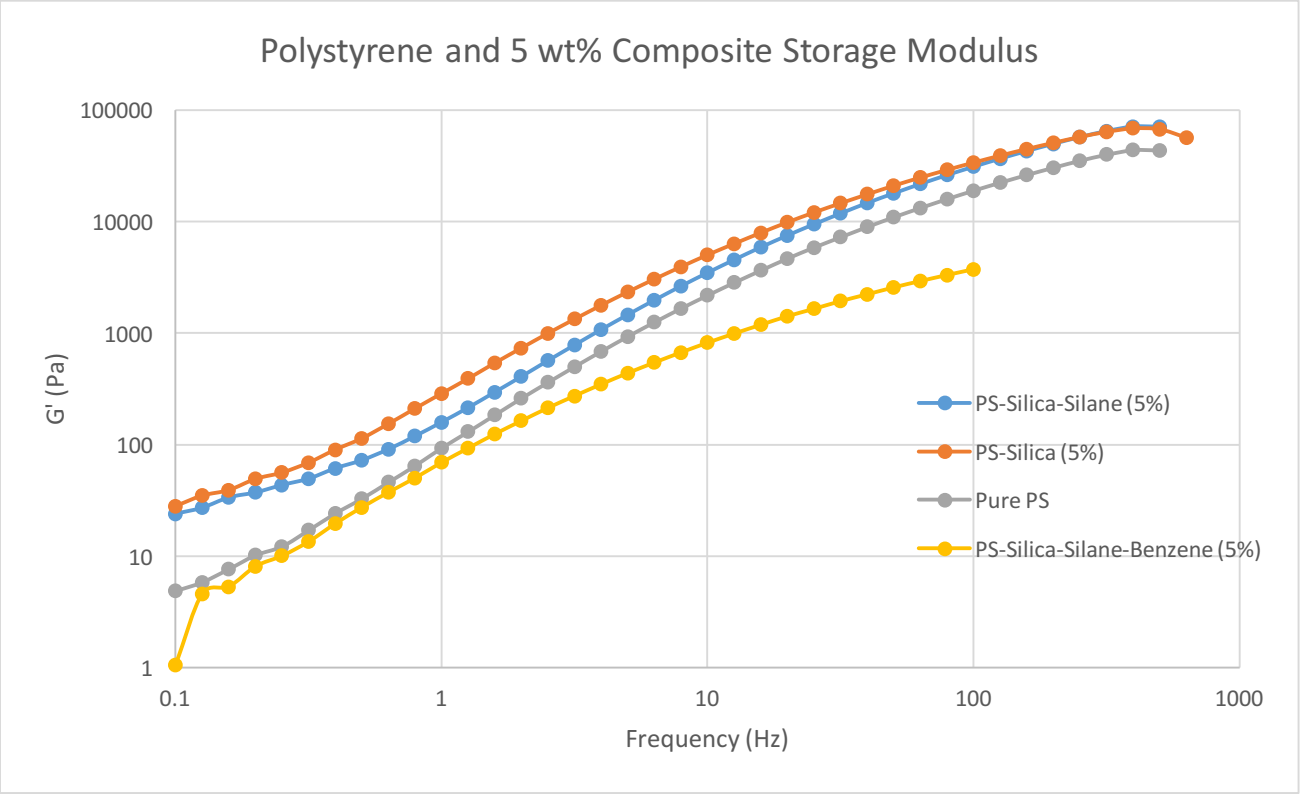

Figure 14: G' versus frequency for polystyrene and 5 wt% silica with and without benzene

As seen in Figure 14 above, the composites show greater storage moduli at a greater weight percentage in comparison to previous results. This is consistent with the results found previously. However, the composite with silane coated silica particles have a lower storage modulus in comparison to the composite with silica. The benzene treated silica show even worse results. It is clear that another coupling agent that pairs well with polystyrene is needed.

C. Rheological Testing for Polybutadiene and Silica Composites

Testing was also performed replacing polystyrene with polybutadiene which is more similar to the commonly used SBR in tires. Ideally, the polystyrene would produce curves that are closer to what can be found in industry.

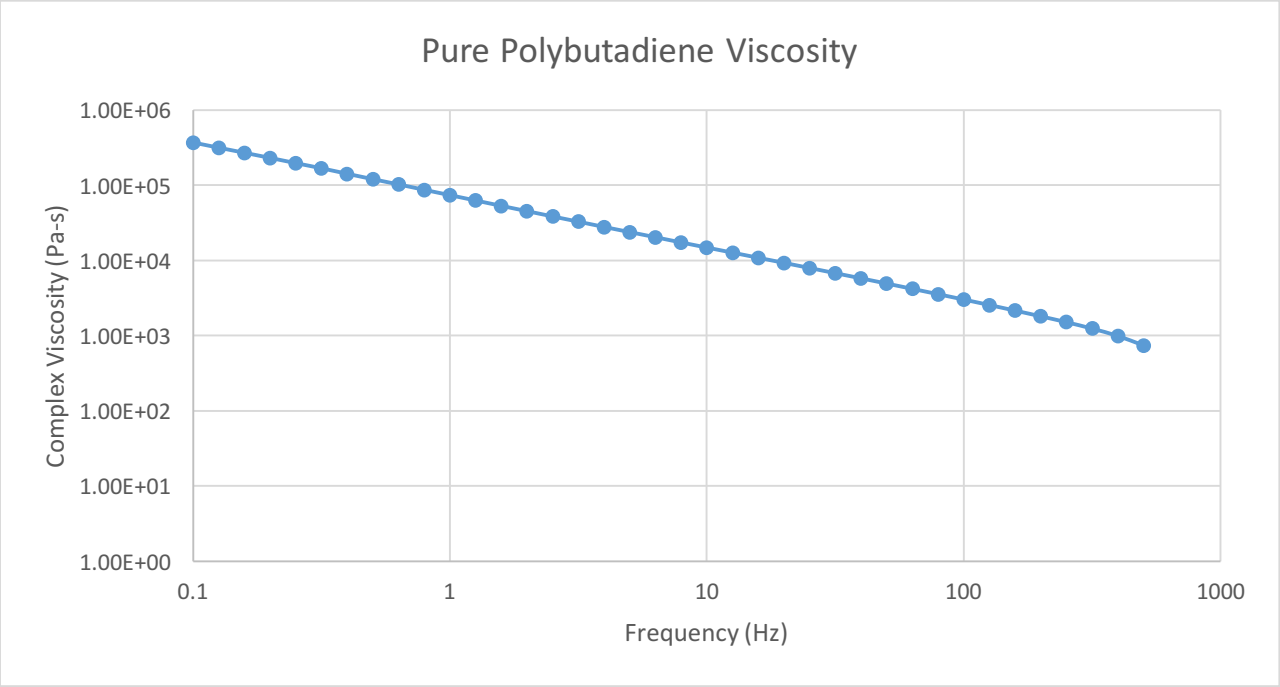

Figure 15: Complex viscosity versus frequency for pure polybutadiene

As seen in Figure 15 above, the complex viscosity significantly decreased with frequency. As frequency or shear rate increased, the viscosity decreased. This is consistent with shear thinning behavior in viscoelastic materials.

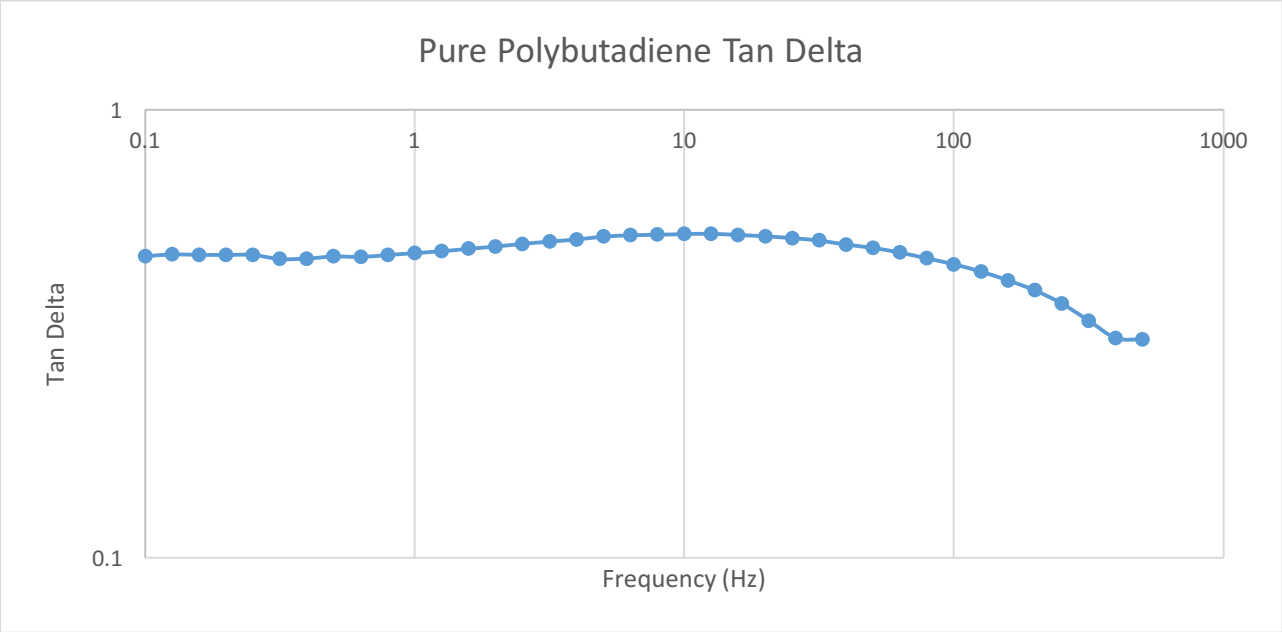

Figure 16: Tan delta versus frequency for pure polybutadiene

As seen in Figure 16 above, the tan delta value decreased with frequency. Tan delta for pure polybutadiene was much lower in comparison to pure polystyrene. The pure polybutadiene stores energy at low frequencies, which is ideal for rolling resistance. However, energy is stored at high frequencies as well which is not ideal for grip.

Silica particles were added to the polybutadiene at varying weight percentages to improve the rheological properties desired. The results were compared to the pure polystyrene data.

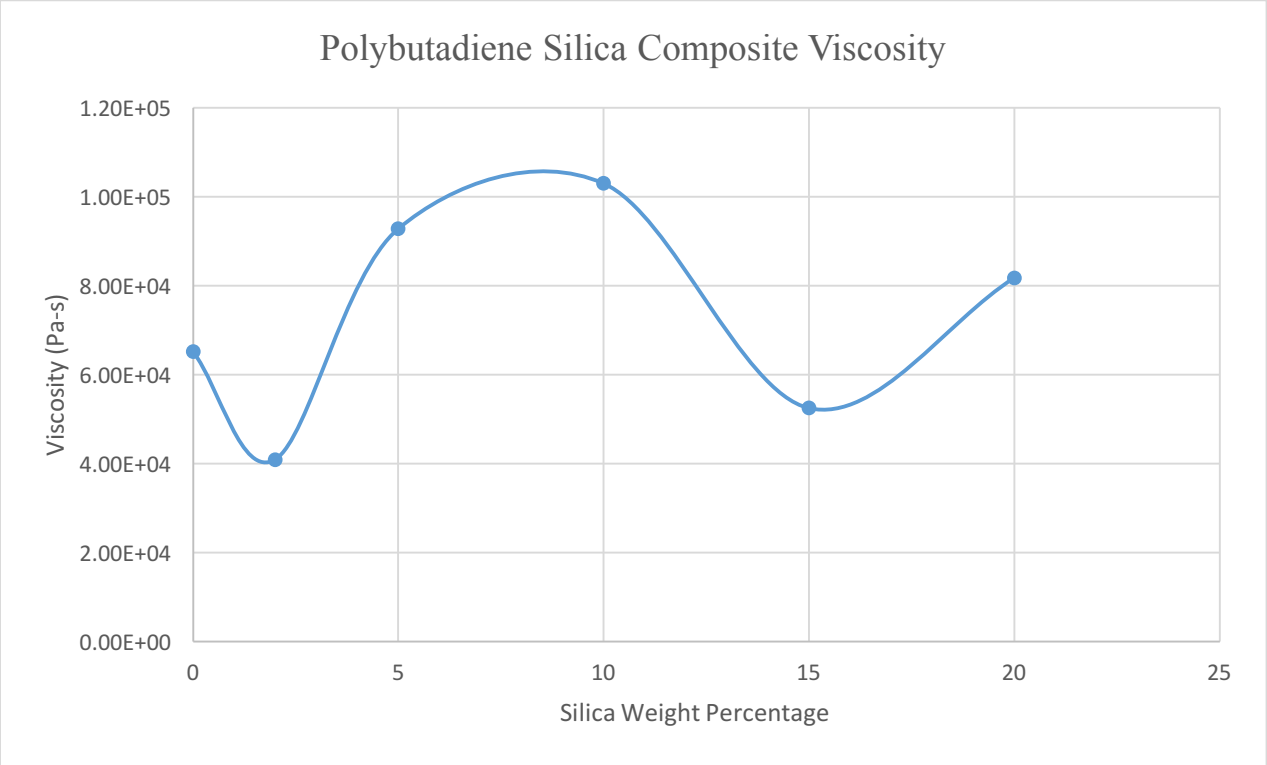

Figure 17: Viscosity versus silica weight percentages for polybutadiene and silica

As seen in Figure 17 above, unfortunately, the polybutadiene data was inconclusive at all weight percentages. When plotting the viscosity vs. silica weight percentage, no trend was found. For polystyrene, viscosity generally increased as the silica weight percentage was increased, but the polybutadiene shows no such trend.

Similar graphs for polybutadiene were plotted to analyze trends in the storage modulus with the addition of silica and silane coupling agents.

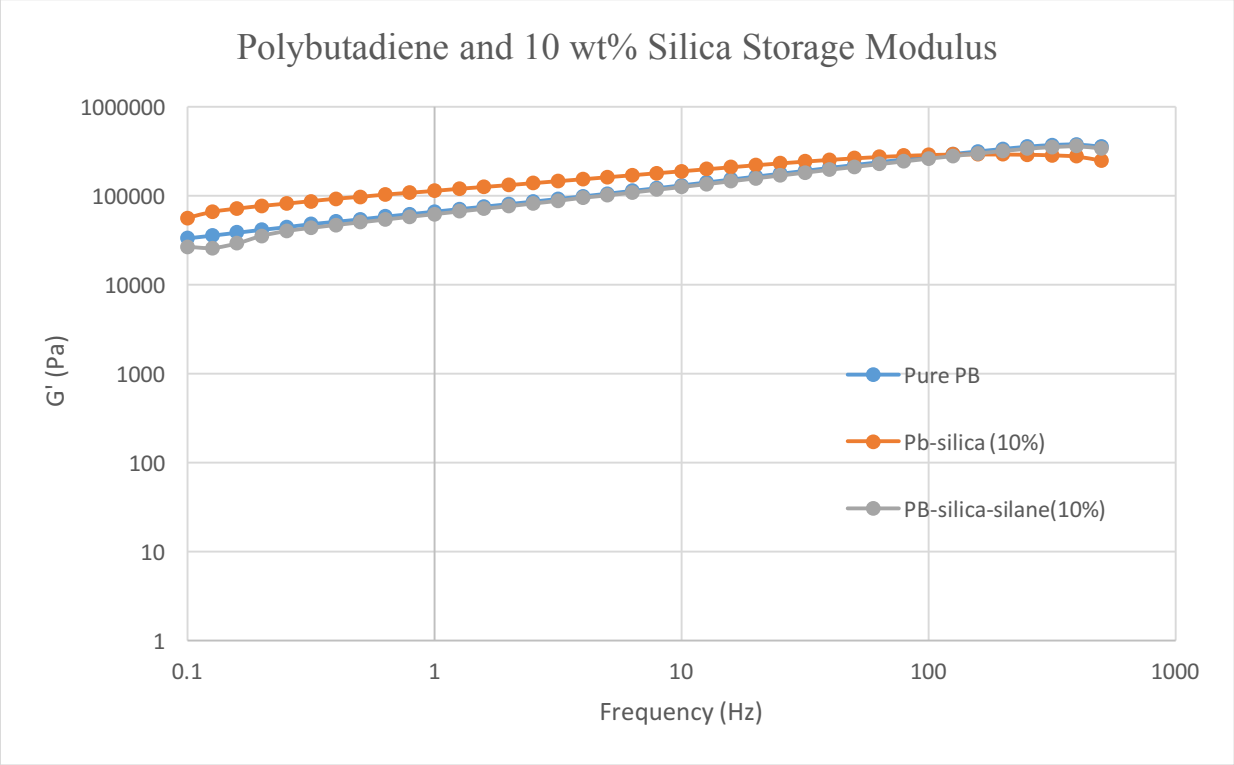

Figure 18: Storage modulus versus frequency for polybutadiene and 10 wt% silica

As seen in Figure 18 above, the storage modulus increased as frequency increased. However the differences are not as extreme in comparison to the polystyrene. There were no significant differences in the graph when adding silica or silane coupling agent. The results are inconclusive because no change occurred when adding nanoparticles. Trends should behave similar to polystyrene as expected. Varying weight percentages also exhibit similar inconclusive data and can be found in the Appendix.

It is possible that the inconclusive polybutadiene data can be attributed to the polybutadiene degrading within the extruder. The polymer chains may have been broken under high shear rates from the rotating screws. When experimenting, it was observed that the screws had a difficult time turning when higher weight percentages of silica were used. A two roll mill

with low shear rates may be used in the future in order to prevent the polybutadiene from degrading when blending.

D. Modeling for Polystyrene and Silica Suspensions

In order to determine how close the viscosity of the polystyrene and silica composite compared to typical suspensions with spherical particles, the data was fitted to various models.

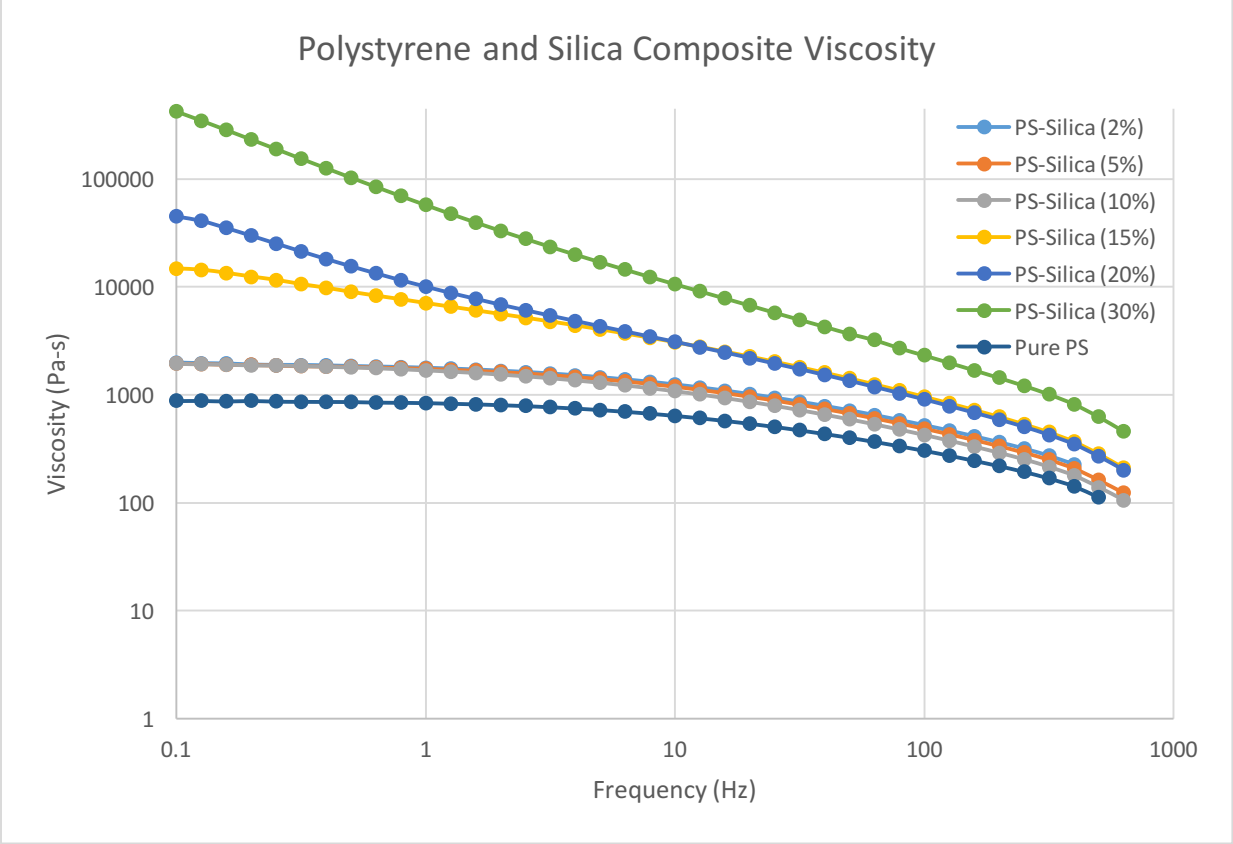

Figure 19: Viscosity versus frequency for polystyrene and silica and varying weight percentages

As seen in Figure 19 above, as the weight percentages (proportional to volume fraction) increased, the viscosity of the material also increased. The silica showed a significant effect on the viscosity of the material at low frequencies. The zero or low shear viscosity (at 0.1 Hz) was used for the values on the model below. However, at high volume fractions, the zero shear

viscosity is not reached at 0.1 Hz. Unfortunately, the rheometer does not test low enough frequencies in order to determine the exact value.

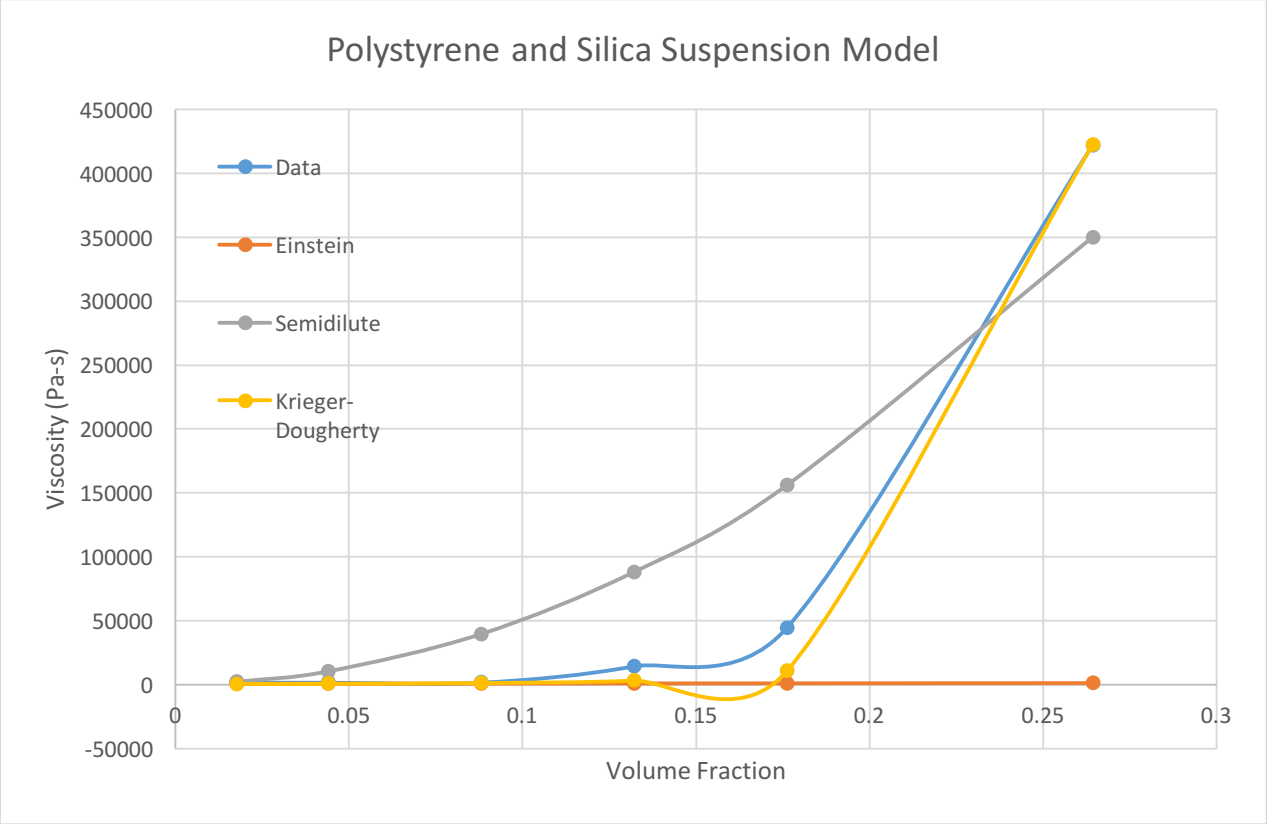

Figure 20: Models for Polystyrene and Silica Suspension

As seen in the Figure 20 above, three different models were fitted to the data based on the following equations (Einstein, Semi-Dilute, Krieger-Dougherty). A curved line was connected in between data points to provide a better visual representation of the model.

$$\eta_r = 1 + B\phi,$$

$$\eta_r = 1 + B\phi + B_1\phi^2 + \cdots,$$

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-B\phi_m}$$

Typically, for the linear Einstein model, the B value is 2.5 for spherical particles suspended in the solvent (polystyrene) [7]. The Einstein model for dilute suspensions (volume fraction < 0.01) with a B value of 2.5 has the worst fit on the data. For the Semi-Dilute model (volume fraction < 0.25) , while keeping 2.5 as the linear B value, the B_1 value was found to be 5668. For the Krieger-Dougherty model, the B value was found to be 53. Conclusively, the polystyrene and silica composite does not fit well into models for typical suspensions. The best fit on the data was the Krieger Dougherty model, but there was still substantial error. The zero shear viscosities were tested, however, for high volume fractions, the viscosities were not the zero shear viscosities. Additionally, because of the variability within the samples and inaccuracy of loading the microcompounding, it is unlikely that the volume fractions were accurate.

CONCLUSION AND FUTURE WORK

The primary objective of this research was to explore polymer and nanoparticle interactions that effect rheological properties related to increasing grip while decreasing rolling resistance in tires. For polystyrene and silica, the rheological properties associated with rolling resistance were improved. At low frequencies that correspond with rolling resistance, the storage modulus was significantly improved. Additionally, greater improvements of several orders of magnitude was observed at higher weight percentages of silica. The rheological properties associated with grip were inconclusive. At high frequencies that correspond with grip, the loss modulus remained mostly unchanged. Loss modulus also increased at low frequencies, which is undesirable for rolling resistance. The inconclusive results for grip may be attributed to the low frequencies that were tested by the rheometer. Grip is associated with frequencies from 10^3 and 10^{10} Hz, and the rheometer used in this experiment tested a maximum of 10^3 Hz. It is possible that more changes in loss modulus may be observed at higher frequencies. For polystyrene and silica coated with silane coupling agent, the results were inconclusive. When the silane was tested independently with the polystyrene, it was discovered that the silane may be acting as a plasticizer with the polystyrene, which negates any benefits observed with increased dispersion. The polybutadiene and silica results were also inconclusive. It is possible that the high shear of the twin-screw extruder was breaking the polymer chains which resulted in irregular results.

For future work, because the rheometer is unable to record data beyond 10^3 Hz frequencies, time-temperature superposition may be used in order to expand the frequency regime. More data can be collected at high frequencies that correspond to grip. Additionally, a coupling agent that is compatible with polystyrene may be used in order to analyze the benefits of increased dispersion within the polymer nanocomposite. Lastly, a two roll mill may be used in

the polybutadiene experiments to ensure that high shear when blending the polybutadiene and silica do not break the polymer chains that result in inconclusive data.

REFERENCES

[1] Modern Tire Dealer. 2015 Facts Issue. (2015). http://www.moderntiredealer.com/uploads/stats/mtd-facts-issue- 2015.pdf.

[2] *The Tire Grip*. Clermont-Ferrand: Société De Technologie Michelin, 2001.

[3] National Highway Transportation and Safety Administration. Replacement Tire ConsumerInformation Program: Part 575.106, Final Regulatory Impact Analysis.

[4] "SBR Rubber Supplier, Manufacturer Styrene Butadiene Rubber." *Plastic Extrusion, Rubber Extrusion, Rubber Molding, Rubber Sheet*. N.p., n.d. Web. <http://www.viprubber.com/page/technical_sbr>.

[5] Dinkel, John. "May 2016." Discover Magazine. N.p., n.d. Web. <http://discovermagazine.com/1995/apr/wherethesilicame497>.

[6] Zhuravlev, L. T. "The Surface Chemistry of Amorphous Silica." Colloids and Surfaces (2000): n. pag. Web.

[7] (2010).http://www.nhtsa.gov/staticfiles/rulemaking/pdf/Rolling_Resistance_FRIA.pdf. Mueller, S., E. W. Llewellin, and H. M. Mader. "The Rheology of Suspensions of Solid Particles." Proceedings of the Royal Society 16 Dec. 2009.

[8] Pandey, Y. N., Papakonstantopoulos, G. J. and Doxastakis, M. Polymer/nanoparticle interactions: bridging the gap. *Macromolecules* 46, 5097–5106 (2013).

[9] Kumar, S. K., and Krishnamoorti, R. Nanocomposites: Structure, Phase Behavior, and Properties. *Annual Rev. Chem. Biomol. Eng.* 1, 37-58 (2010).

[10] Bohm, G. A., Tomaszewski, W., Cole, W., and Hogan, T. Furthering the understanding of the non linear response of filler reinforced elastomers. *Polymer* 51, 2057-2068 (2010).

[11] Sarvestani, A. S., and Jabbari, E. Modeling the Viscoelastic Response of Suspension of Particles in Polymer Solution: The Effect of Polymer-Particle Interactions. *Macromol. Theory Sim.* 16, 378-385 (2007).

[12] Ndoro, T. V. M, Böhm, M. C., and Muller-Plathe, F. Interface and Interphase Dynamics of Polystyrene Chains Near Grafted and Ungrafted Silica Nanoparticles. *Macromolecules* 45, 171−179 (2012).

[13] Ghanbari, A., Ndoro, T. V., Leroy, F., Rahimi, M., C. Böhm, M., and Müller-Plathe, F. Interphase Structure in Silica-Polystyrene Nanocomposites: A Coarse-Grained Molecular Dynamics Study. Macromolecules 45, 572−584 (2012).

[14] Fu, X., and Qutubuddin, S. Polymer–clay nanocomposites: exfoliation of organophilic montmorillonite nanolayers in polystyrene. *Polymer* 42, 807-813 (2001).

[15] Tao R. and Simon S. L. Pressure-volume-temperature and glass transition behavior of silica/polystyrene nanocomposite. Journal of Polymer Science Part B-Polymer Physics 53, 1131-1138 (2015).

[16] Tao R. and Simon S. L. Bulk and Shear Rheology of Silica/Polystyrene Nanocomposite: Reinforcement and Dynamics. *Journal of Polymer Science Part B-Polymer Physics* 53, 621-632 (2015).

[17] Zhu, L., Wang, X., Gu, Q., Chen, W., Sun, P. and Xue, G. Confinement-induced deviation of chain mobility and glass transition temperature for polystyrene/Au nanoparticles. *Macromolecules* 46, 2292–2297 (2013).

[18] Mortezaei M., Famili M. H. N., and Kokabi M. The role of interfacial interactions on the glass-transition and viscoelastic properties of silica/polystyrene nanocomposite. *Composites Science and Technology* 71, 1039-1045 (2011).

[19] Herd, C. et al. Use of surface-treated carbon blacks in an elastomer to reduce compound hysteresis and tire rolling resistance and improve wet traction. Patent WO2011028337 A2 (2011).

[20] Vo, L. T., Anastasiadis, S. H., and Giannelis, E. P. Dielectric study of Poly(styrene-co-butadiene) Composites with Carbon Black, Silica, and Nanoclay. *Macromolecules* 44, 6162-6171 (2011).

[21] Wang, R., Yao, H., Lei, W., Zhou, X., Zhang, L., Hua, K., and Kulig, J. Morphology, interfacial interaction, and properties of a novel bioelastomer reinforced by silica and carbon black. *Journal of Applied Polymer Science* 129, 1546–1554 (2013).

APPENDIX

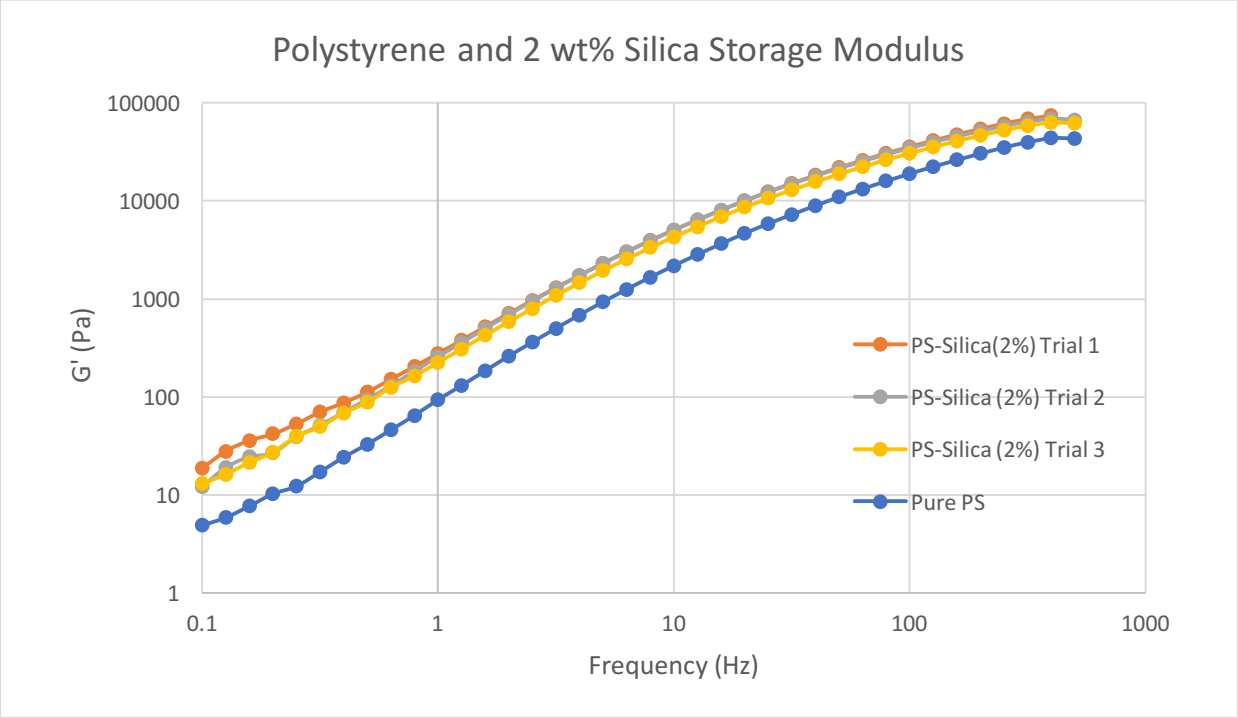

Figure 21: Storage modulus versus frequency for polystyrene and 2 wt% silica

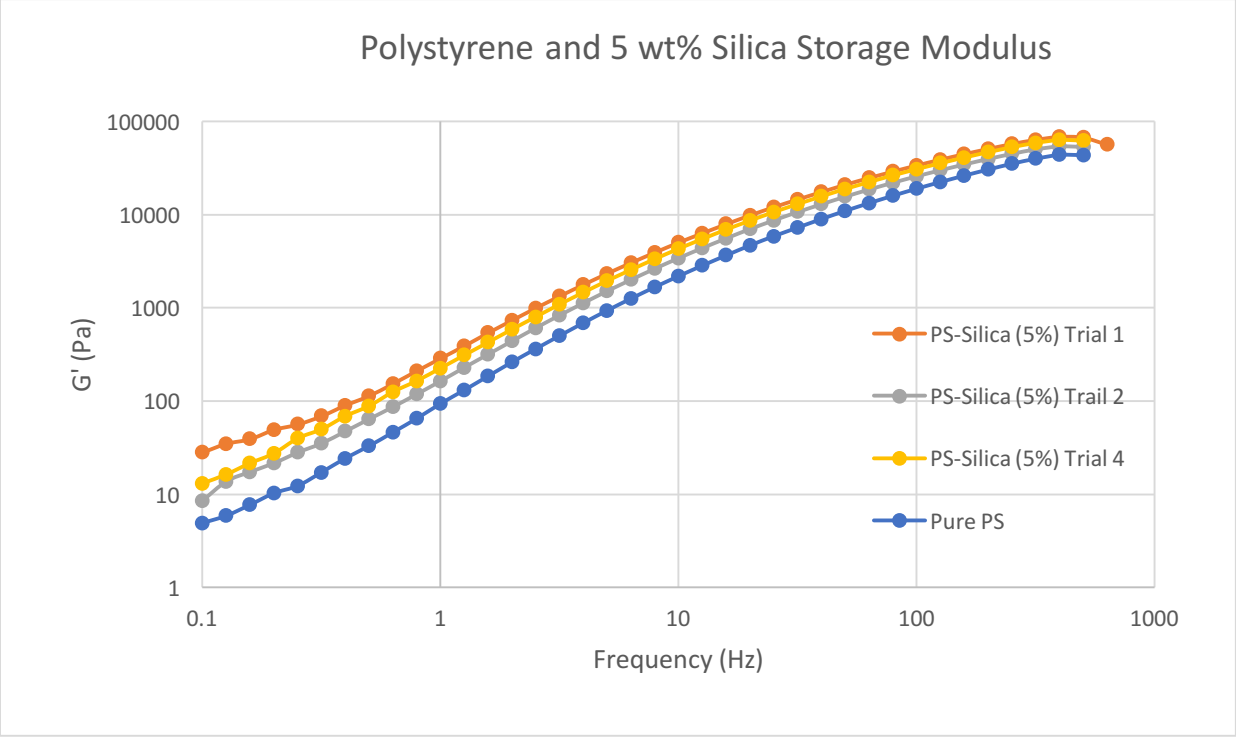

Figure 22: Storage Modulus versus frequency for polystyrene and 5 wt% silica

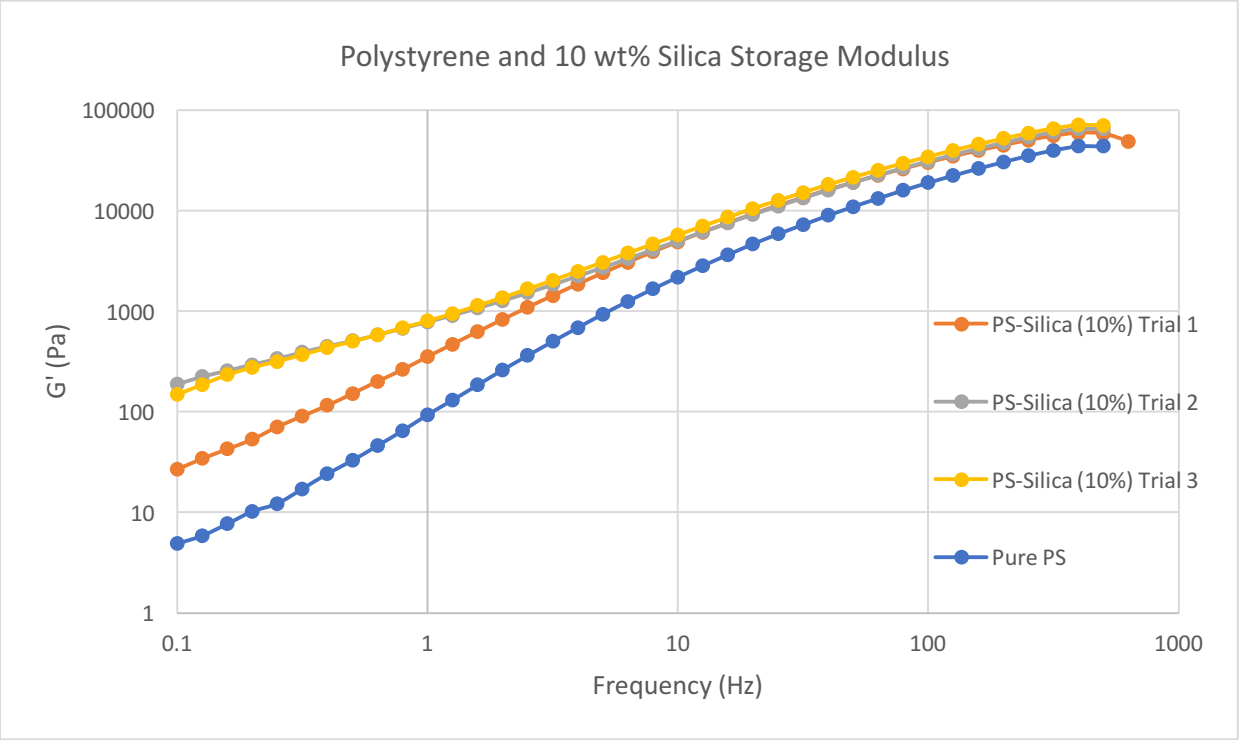

Figure 23: Storage modulus versus frequency for polystyrene and 10 wt% silica

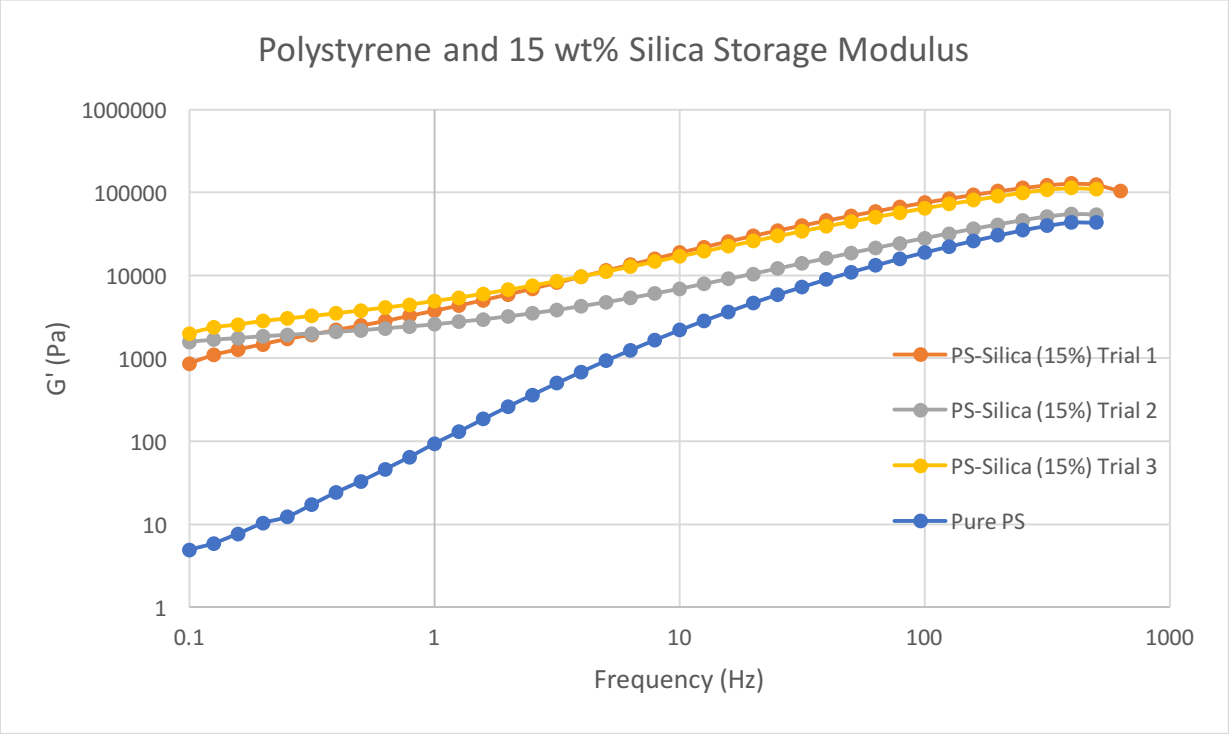

Figure 24: Storage modulus versus frequency for polystyrene and 15 wt% silica

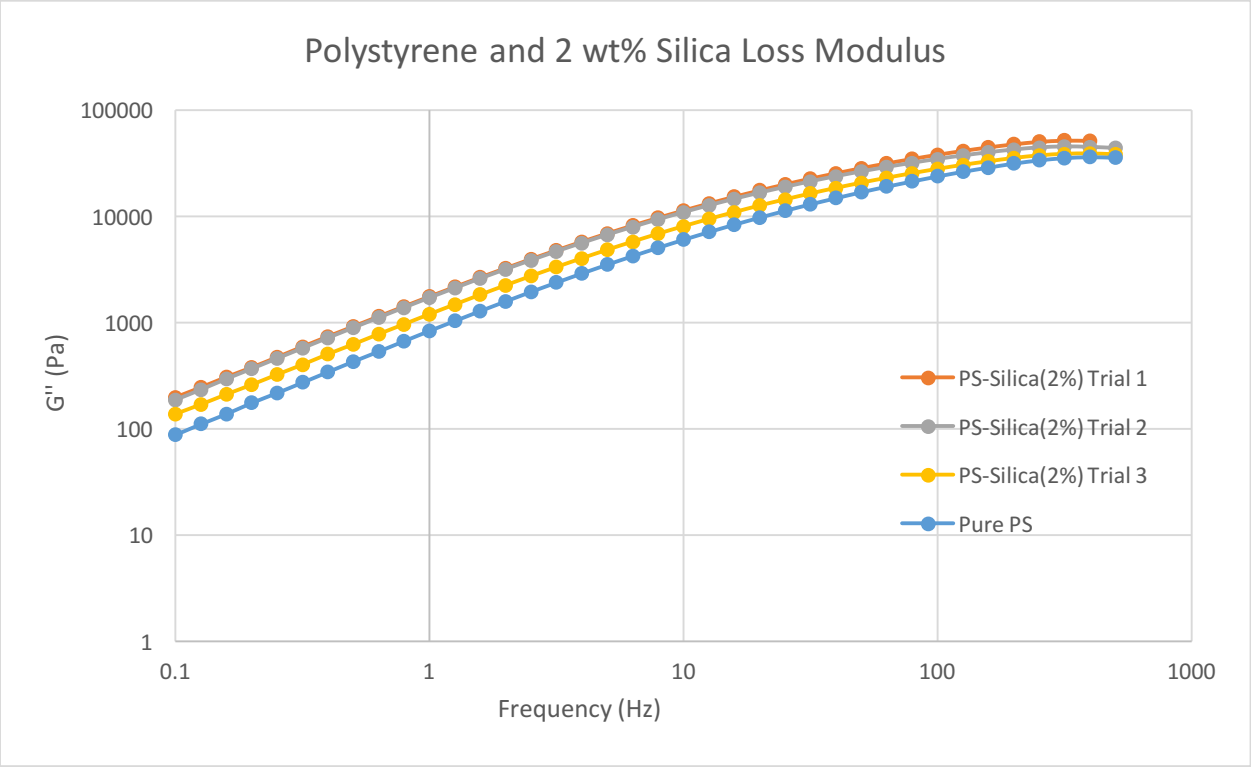

Figure 25: Loss modulus versus frequency for polystyrene and 2 wt% silica

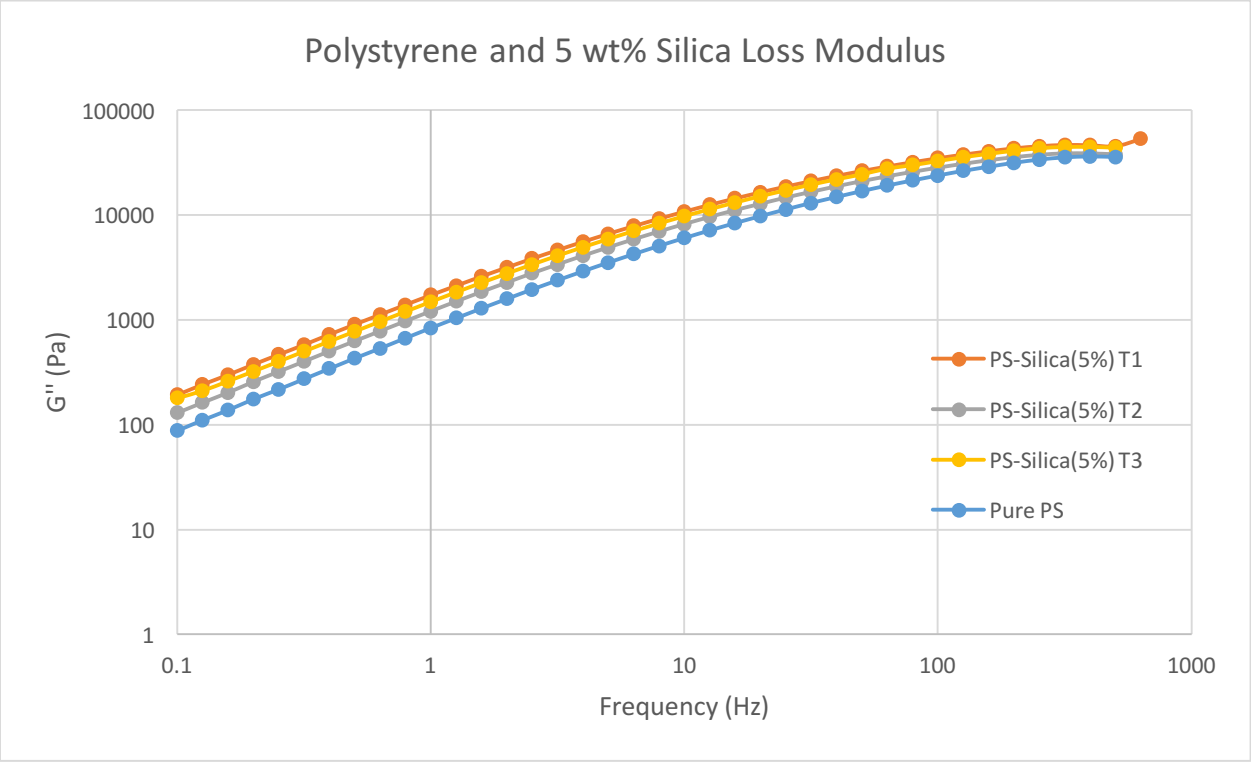

Figure 26: Loss modulus versus frequency for polystyrene and 5 wt% silica

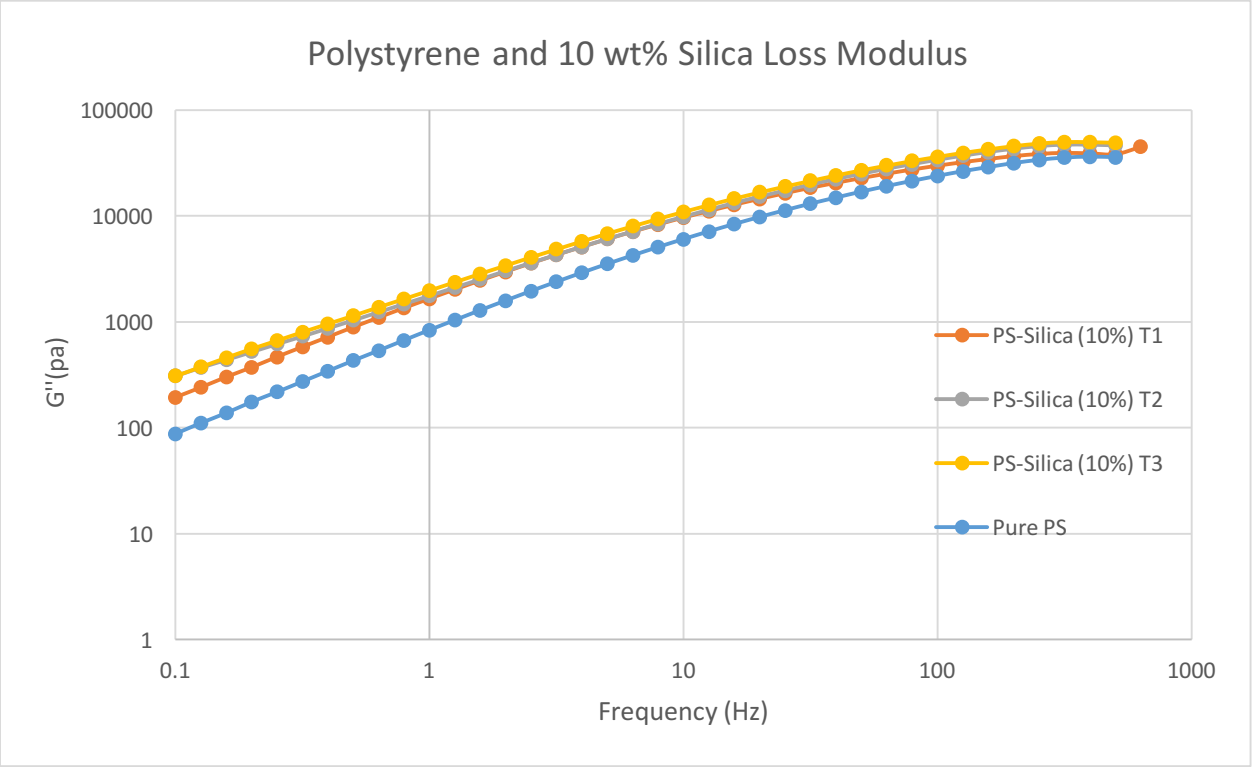

Figure 27: Loss modulus versus frequency for polystyrene and 10 wt% silica

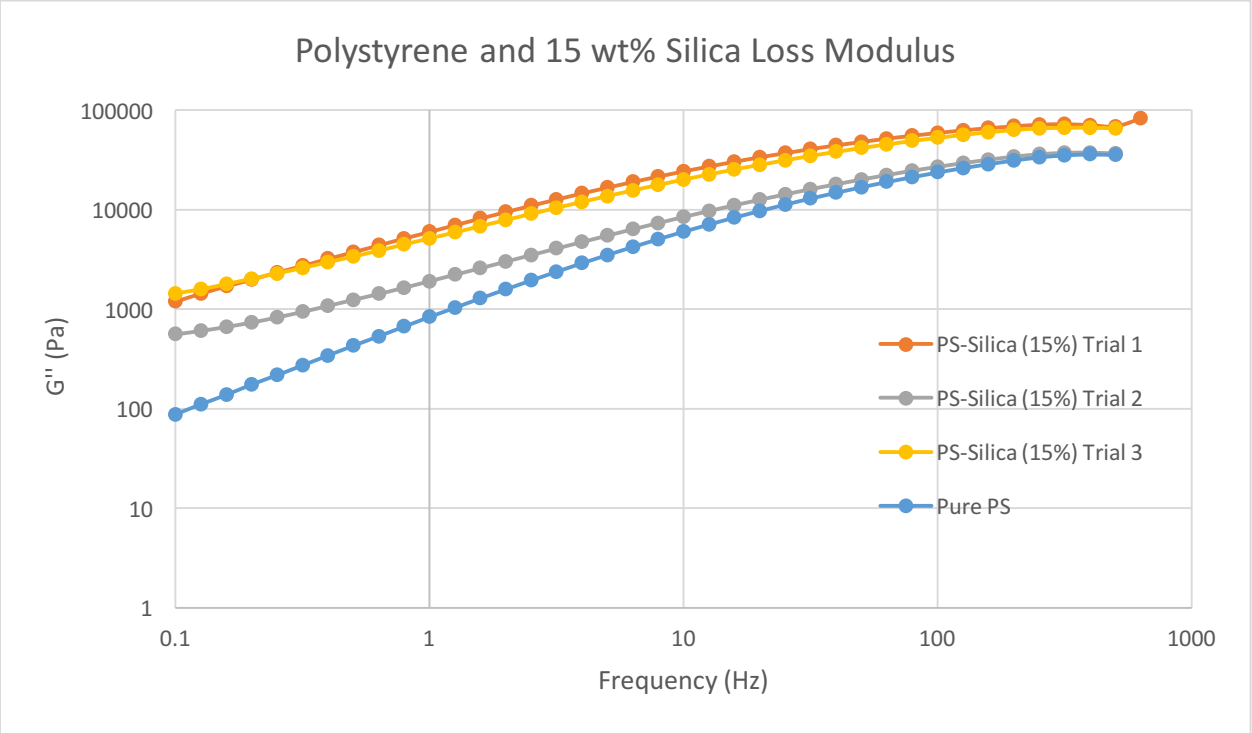

Figure 28: Loss modulus versus frequency for polystyrene and 15 wt% silica

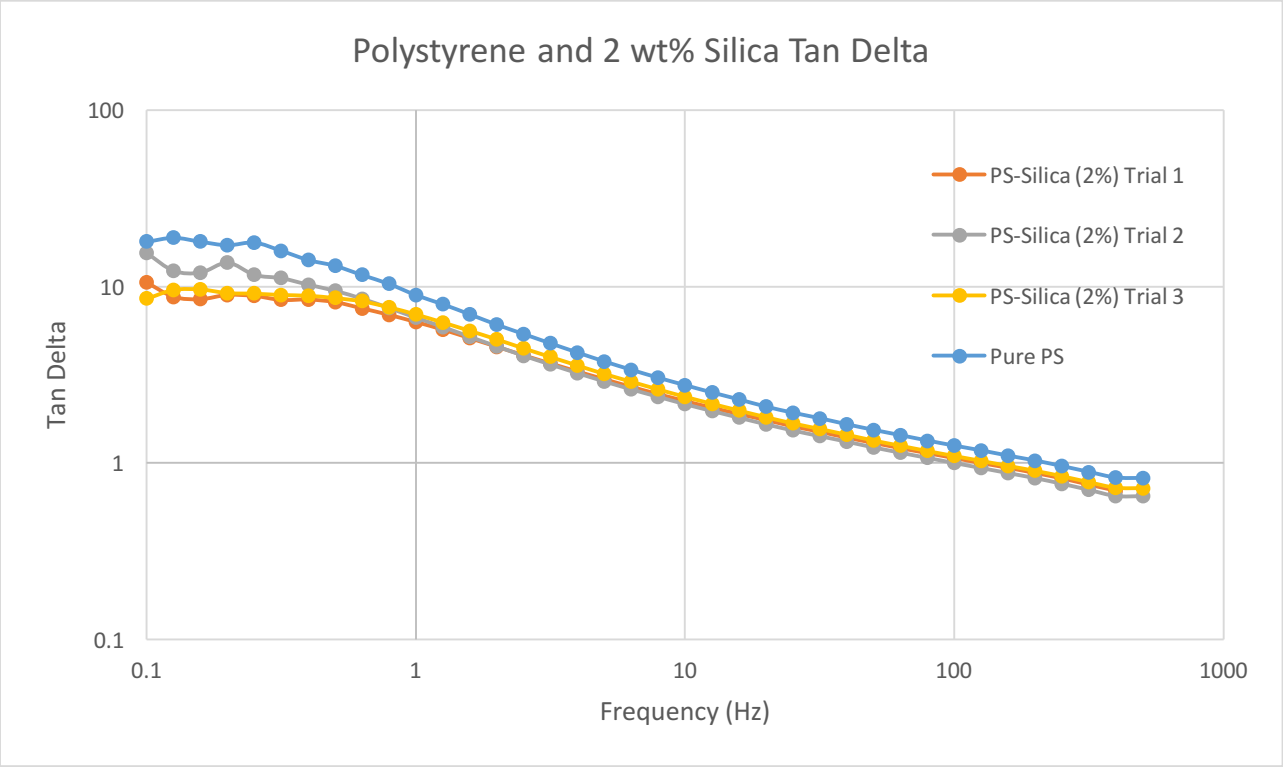

Figure 29: Tan delta versus frequency for polystyrene and 2 wt% silica

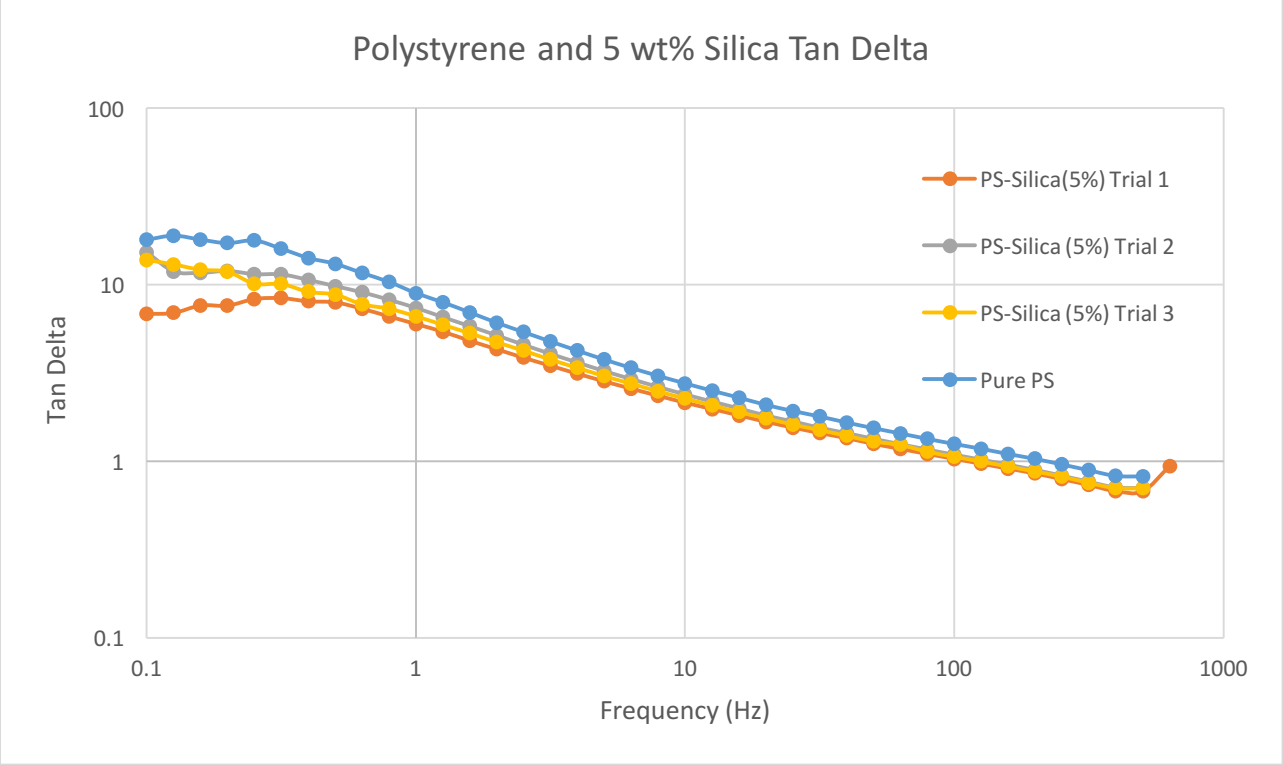

Figure 30: Tan delta versus frequency for polystyrene and 5 wt% silica

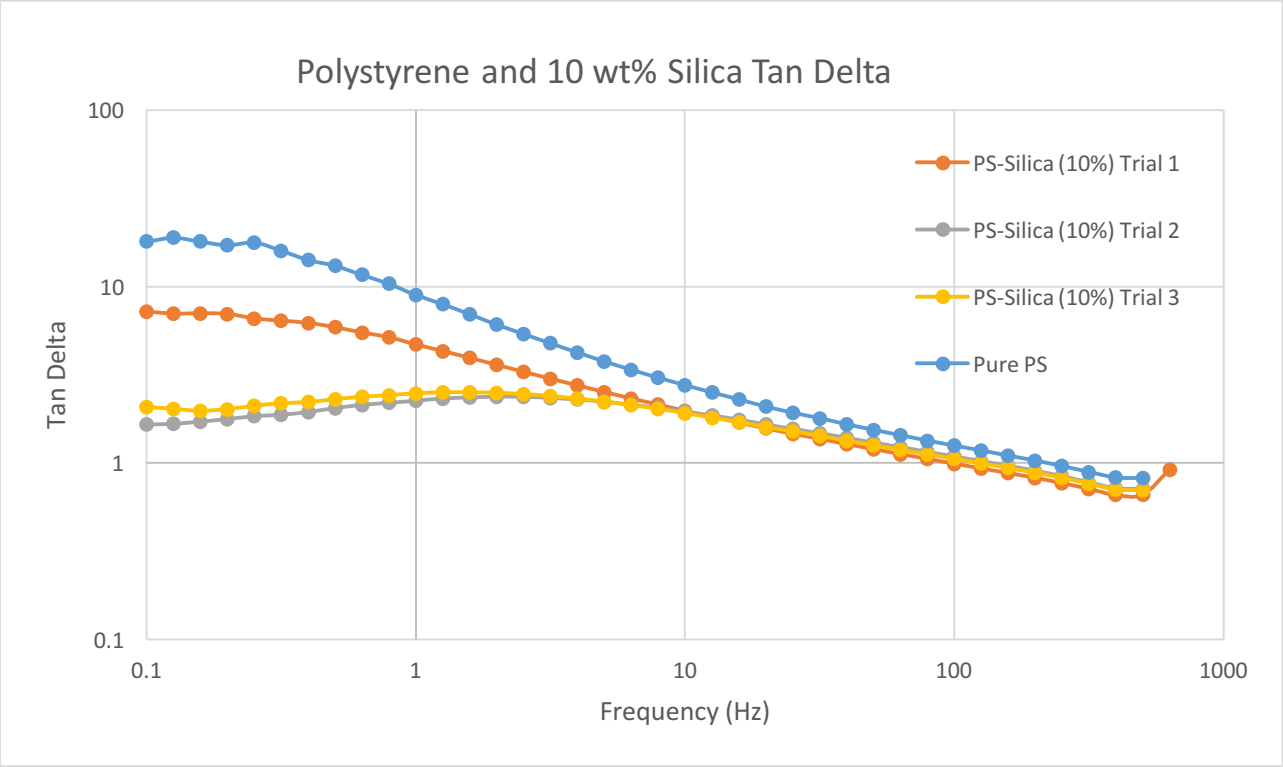

Figure 31: Tan delta versus frequency for polystyrene and 10 wt% silica

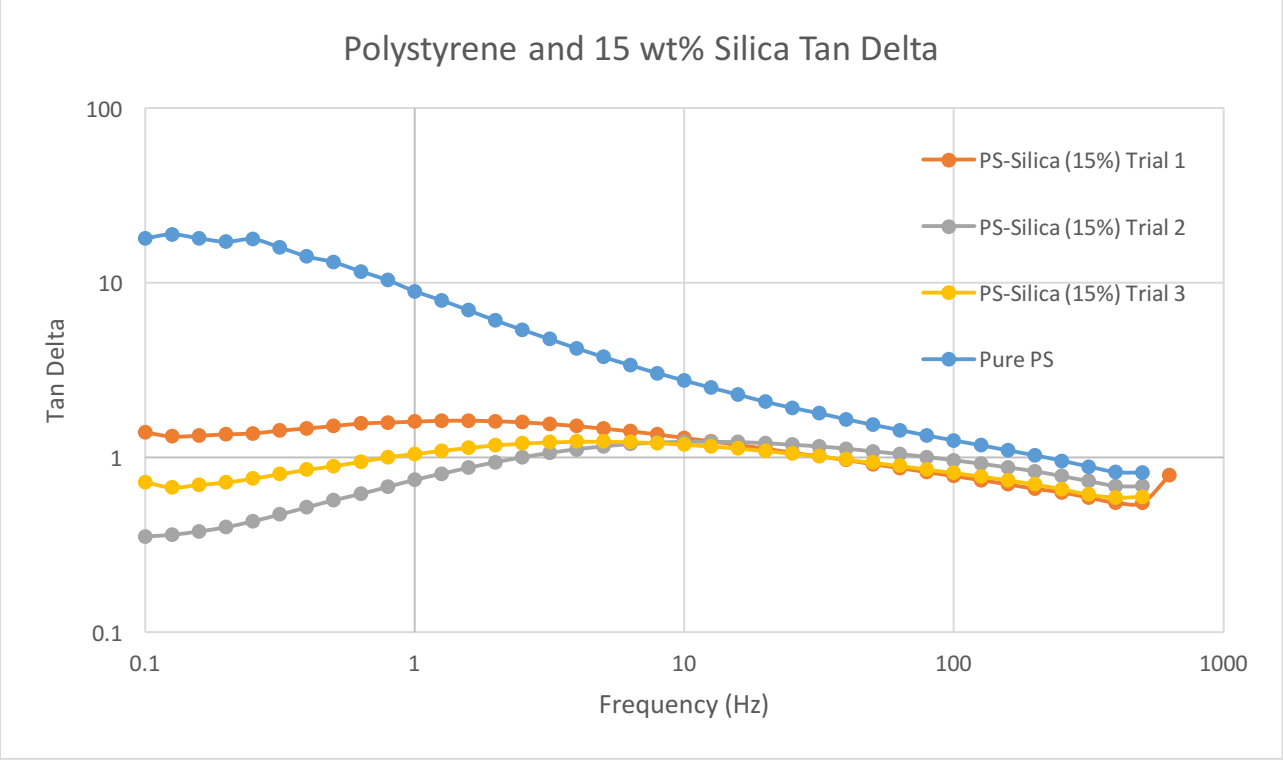

Figure 32: Tan delta versus frequency for polystyrene and 15 wt% silica

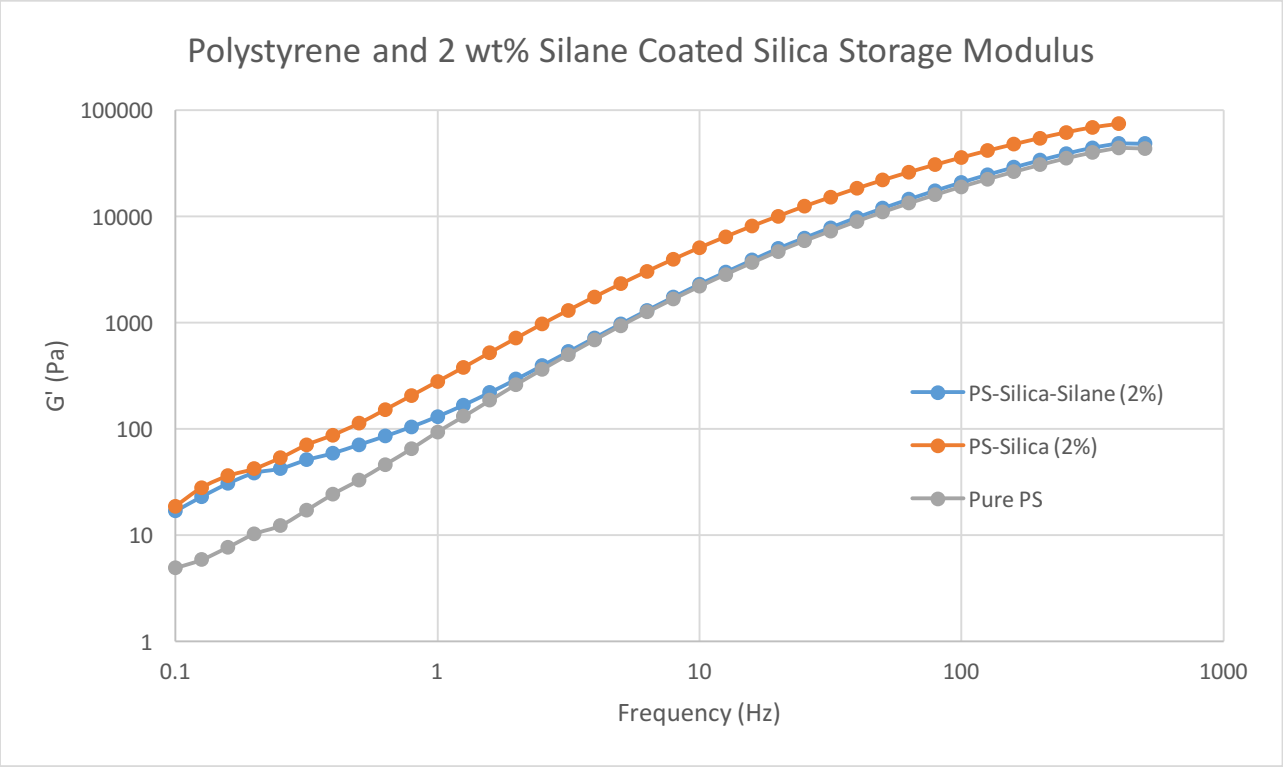

Figure 33: Storage modulus versus frequency for polystyrene and 2 wt% silane coated silica

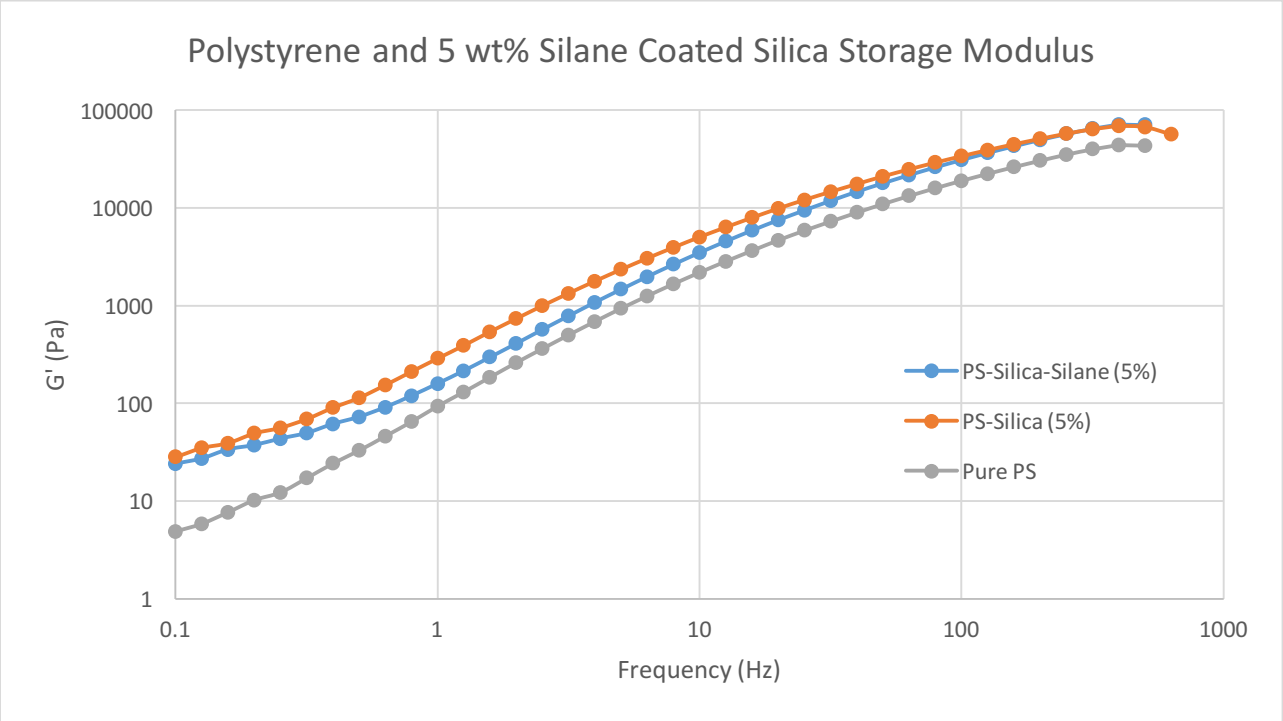

Figure 34: Storage modulus versus frequency for polystyrene and 5 wt% silane coated silica

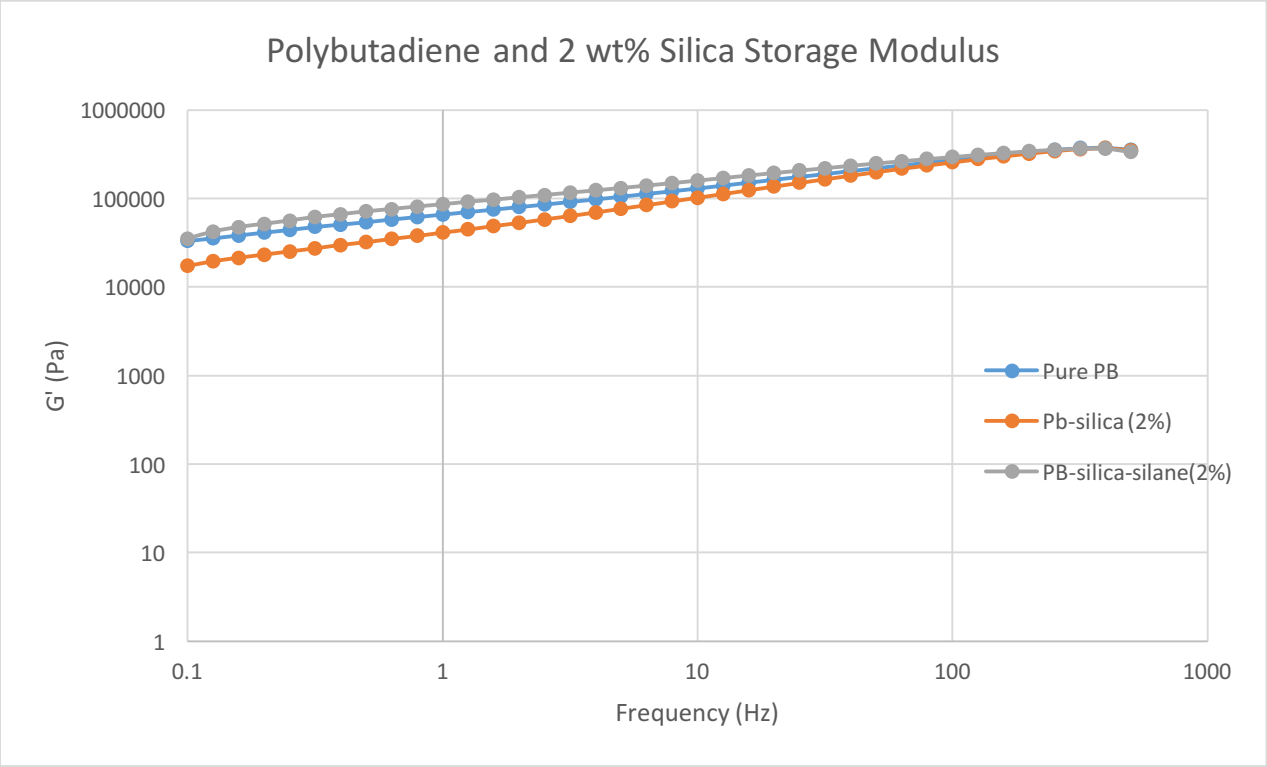

Figure 35: Storage modulus versus frequency for polybutadiene and 2 wt% silica

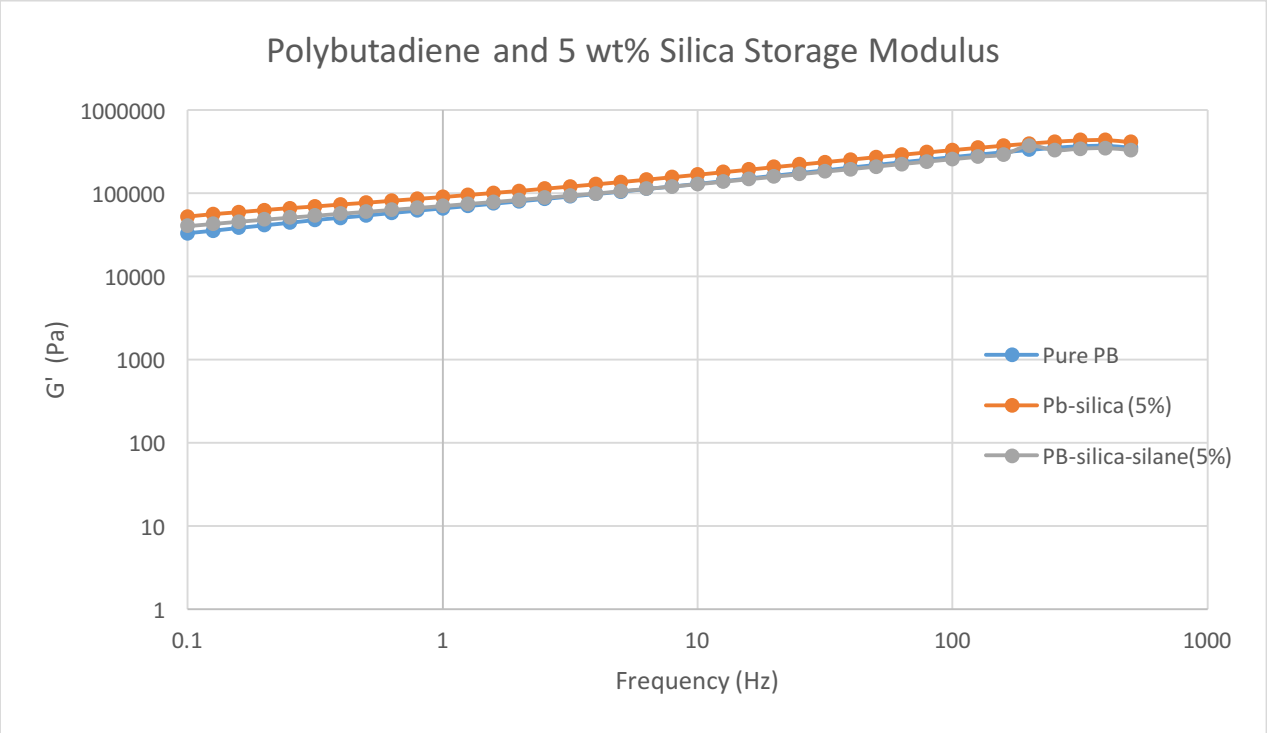

Figure 36: Storage modulus versus frequency for polybutadiene and 5 wt% silica

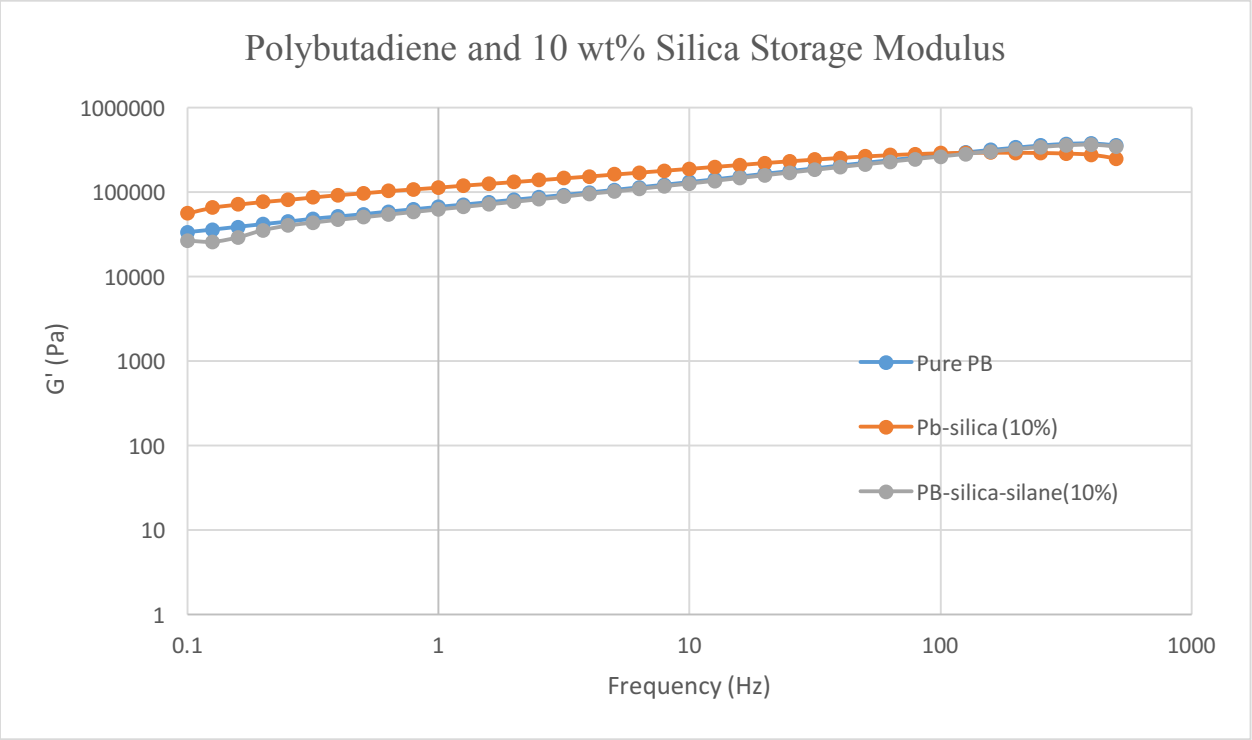

Figure 37: Storage modulus versus frequency for polybutadiene and 10 wt% silica

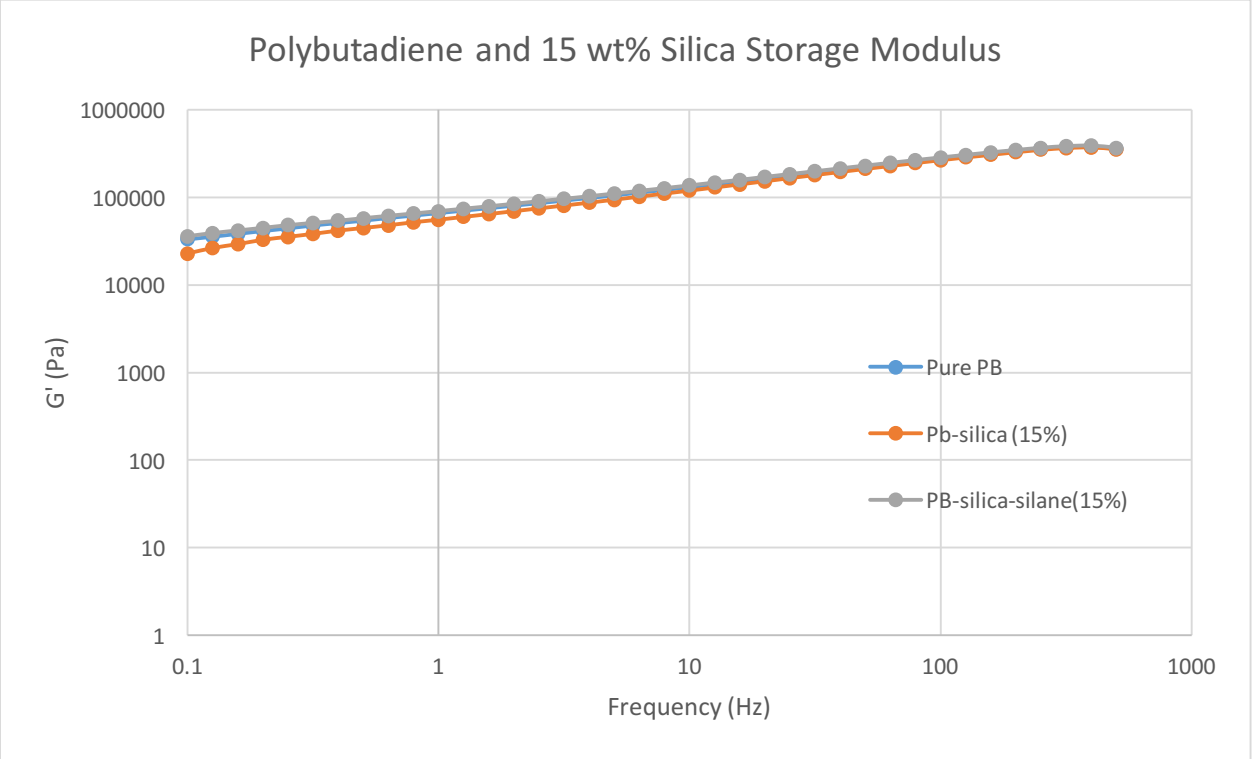

Figure 38: Storage modulus versus frequency for polybutadiene and 15 wt% silica

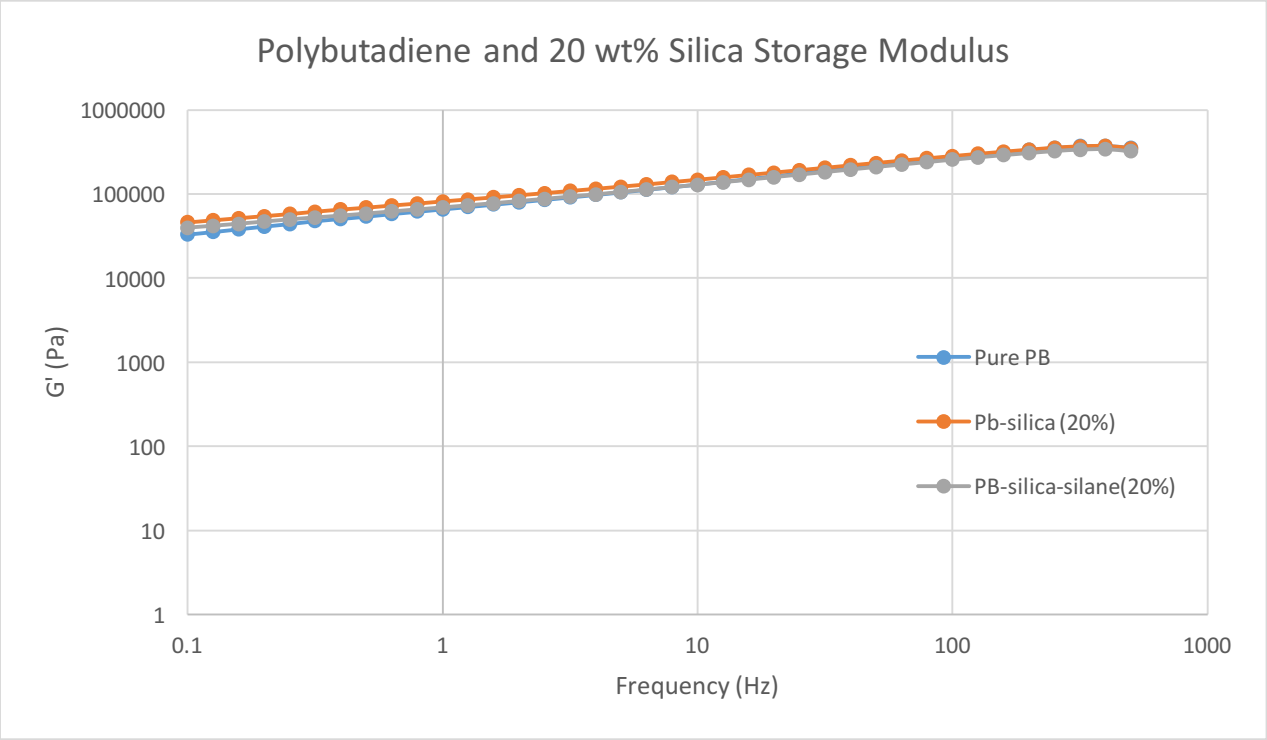

Figure 39: Storage modulus versus frequency for polybutadiene and 20 wt% silica

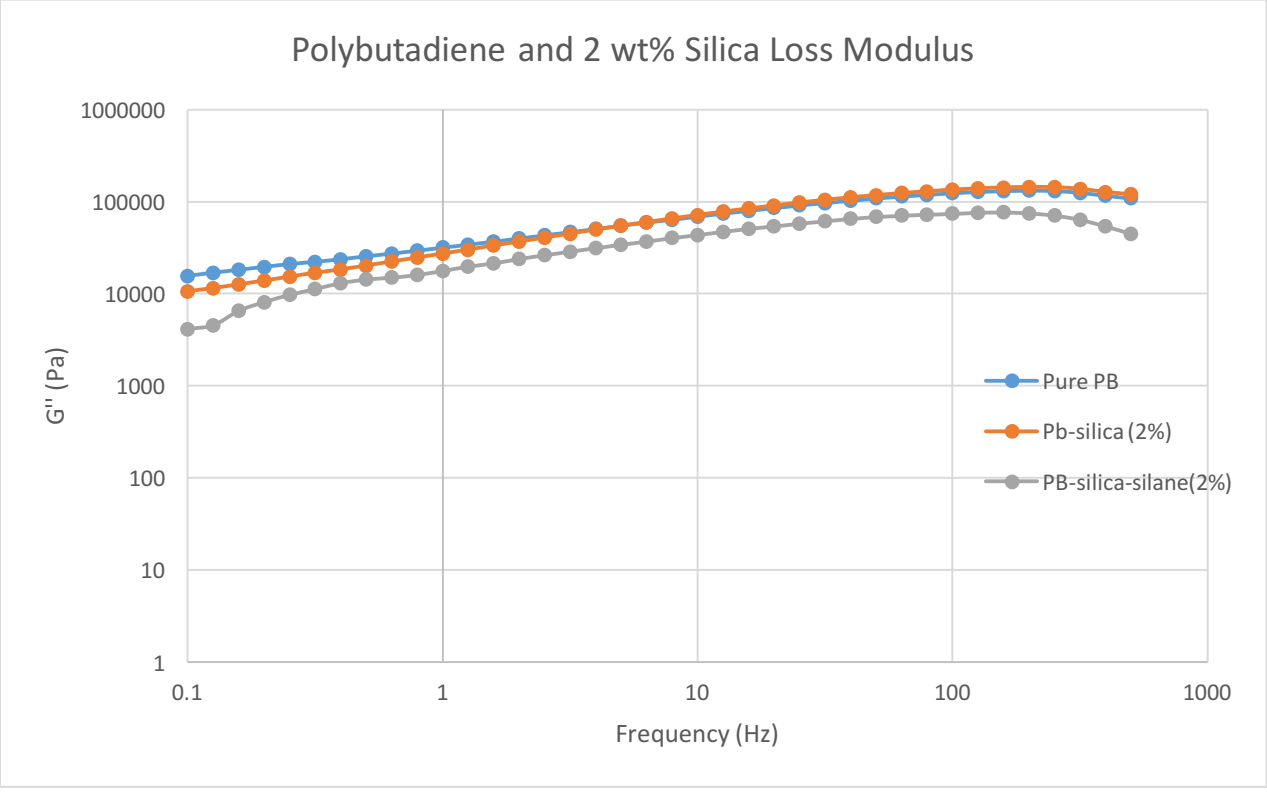

Figure 40: Loss modulus versus frequency for polybutadiene and 2 wt% silica

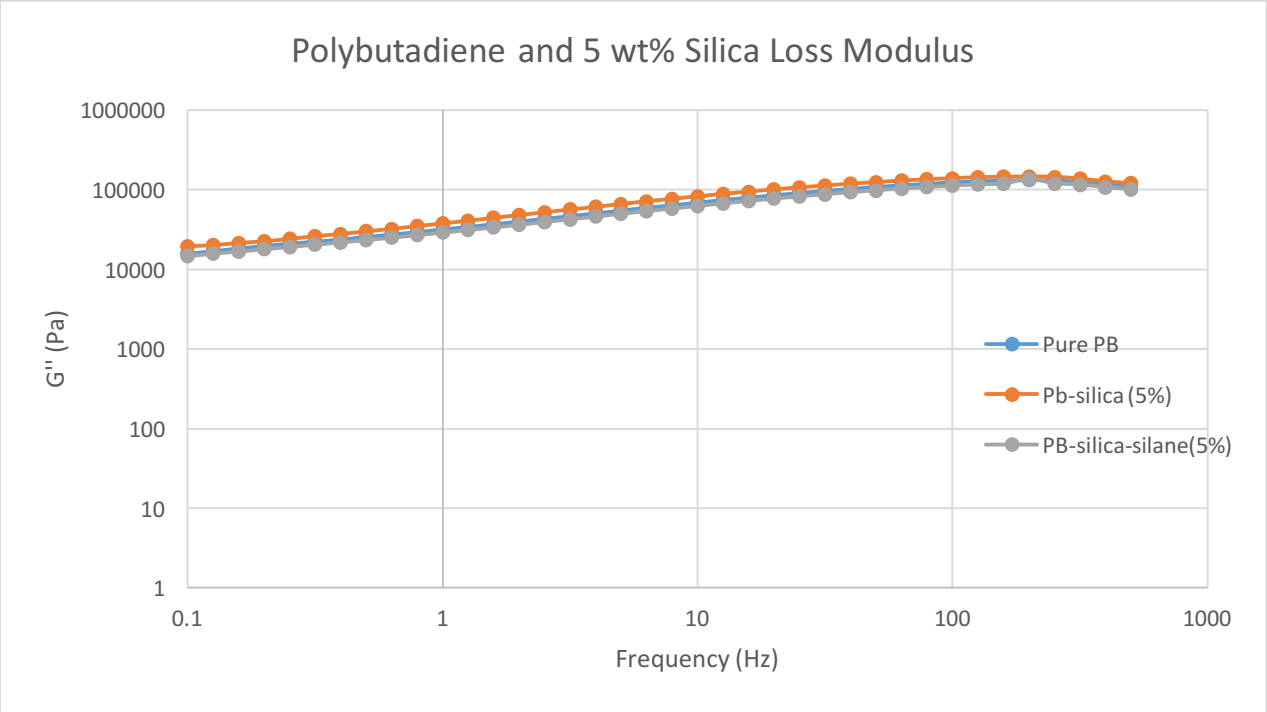

Figure 41: Loss modulus versus frequency for polybutadiene and 5 wt% silica

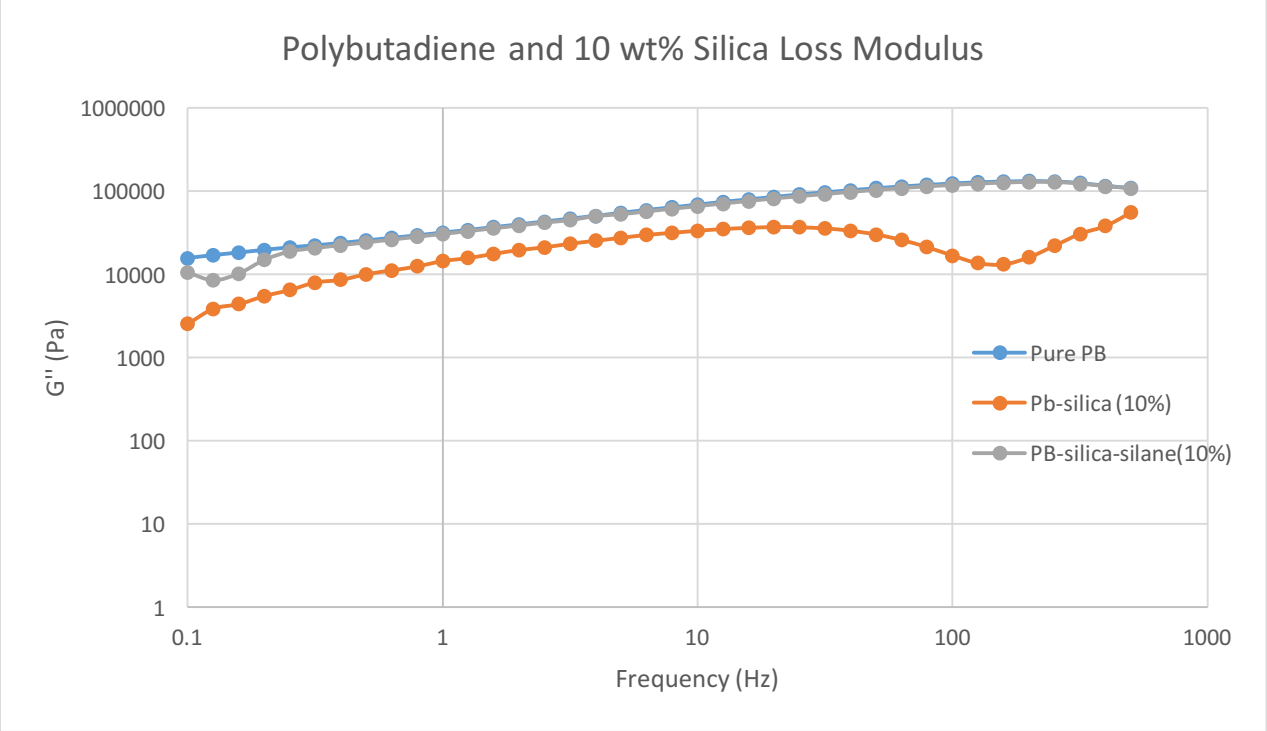

Figure 42: Loss modulus versus frequency for polybutadiene and 10 wt% silica

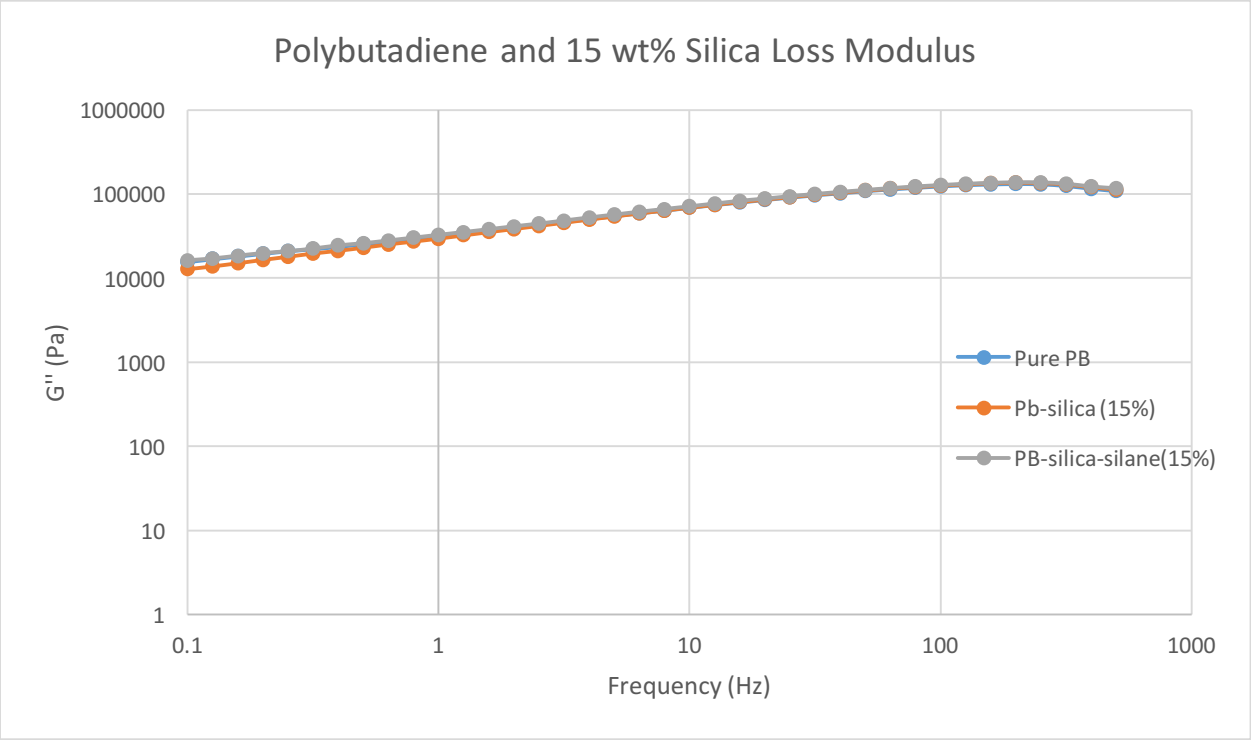

Figure 43: Loss modulus versus frequency for polybutadiene and 15 wt% silica

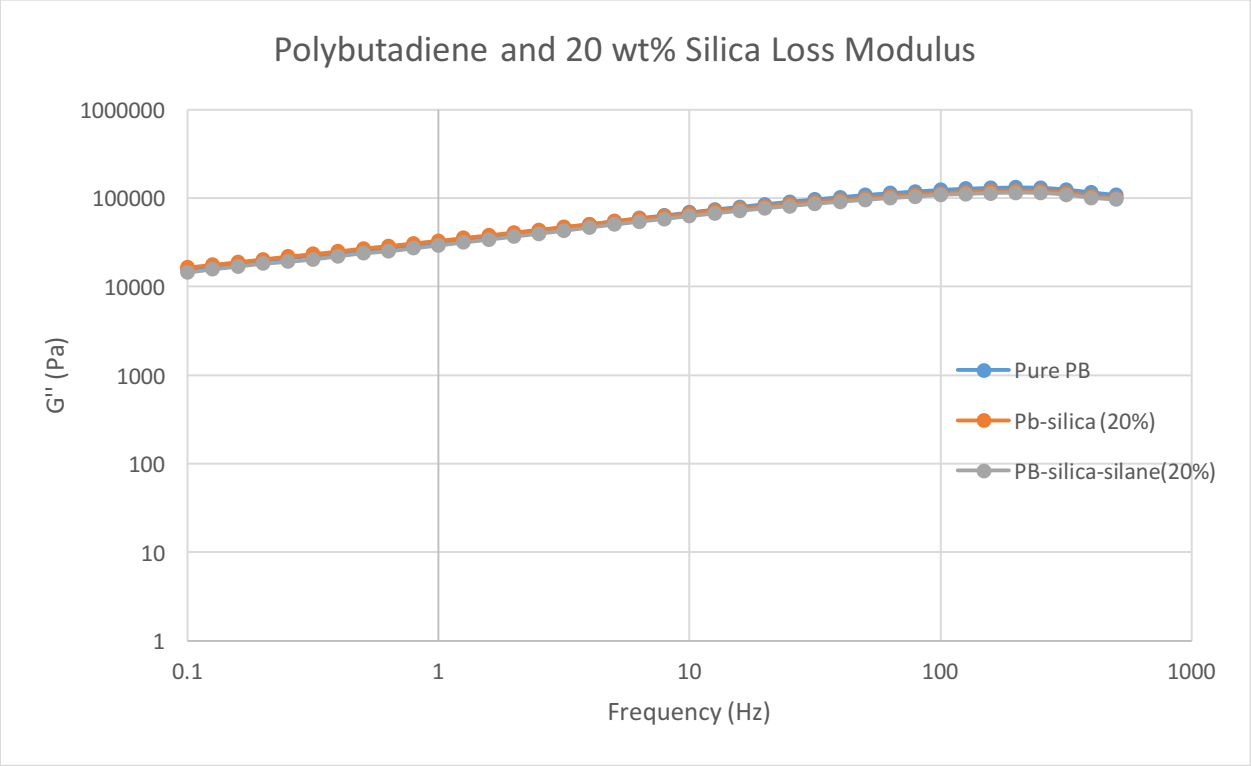

Figure 44: Loss modulus versus frequency for polybutadiene and 20 wt% silica

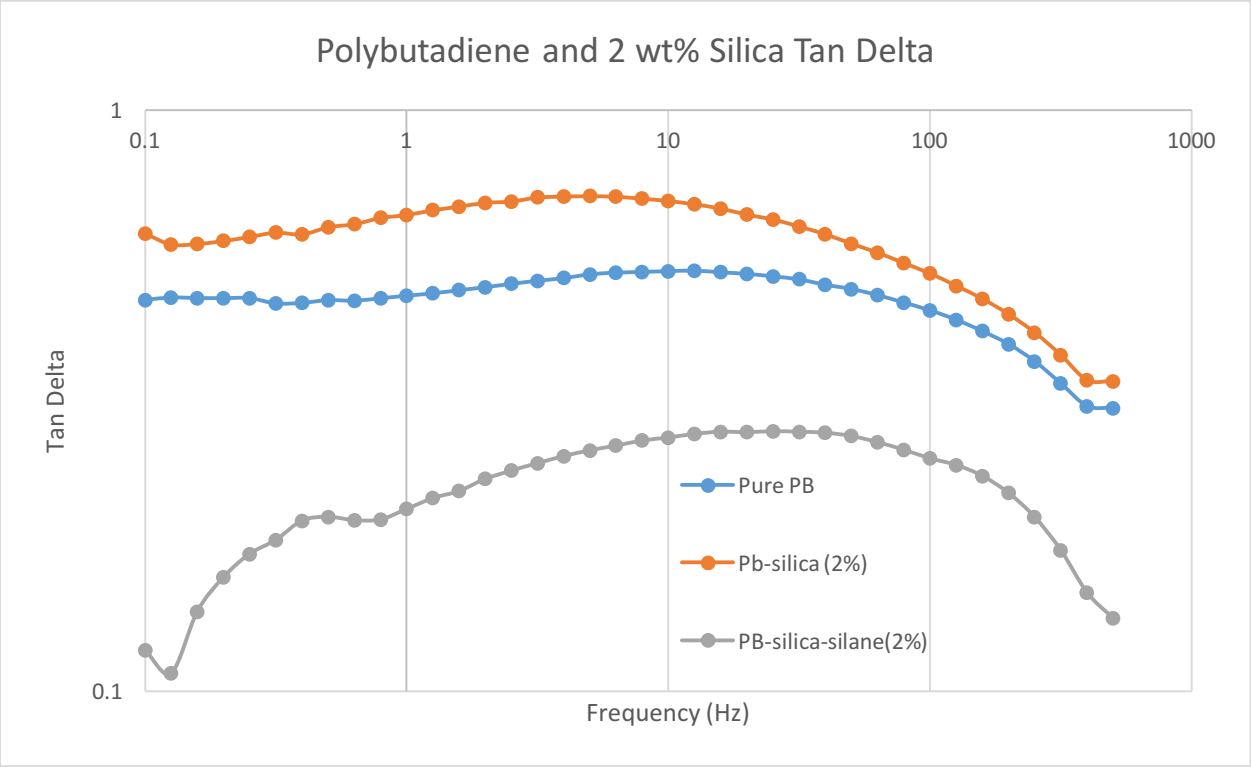

Figure 45: Tan delta versus frequency for polybutadiene and 2 wt% silica

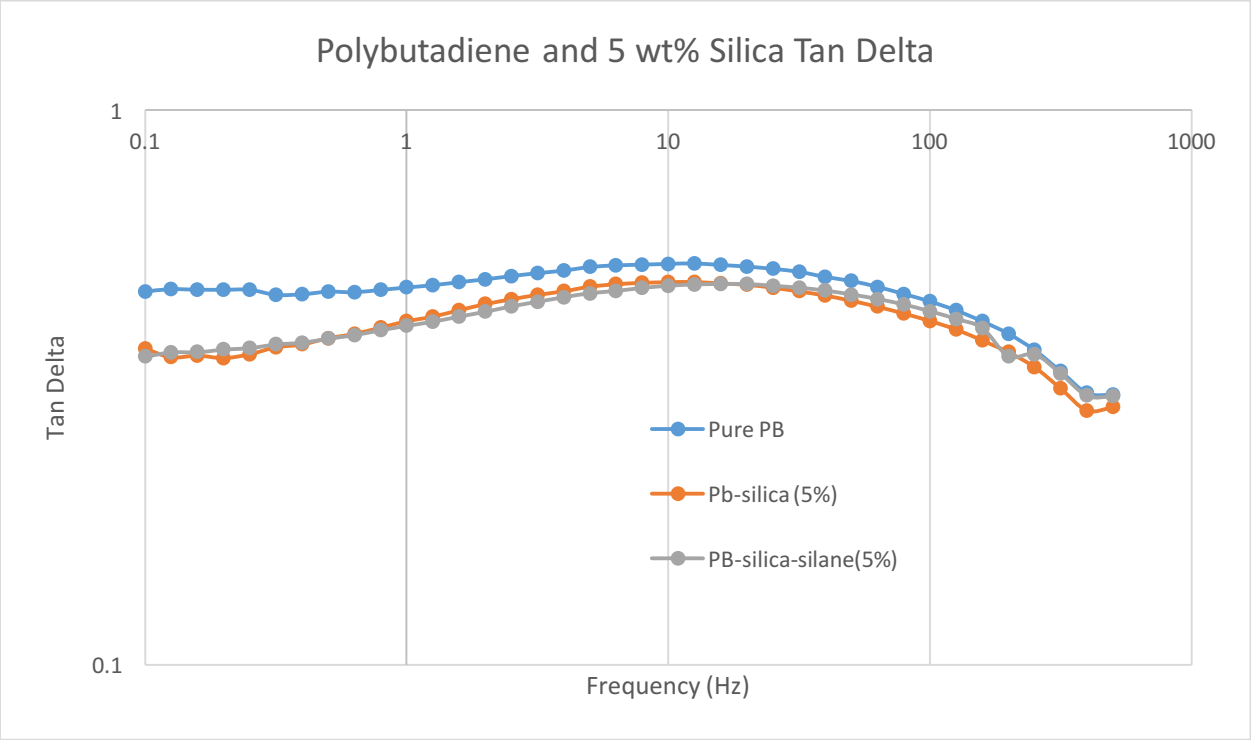

Figure 46: Tan delta versus frequency for polybutadiene and 5 wt% silica

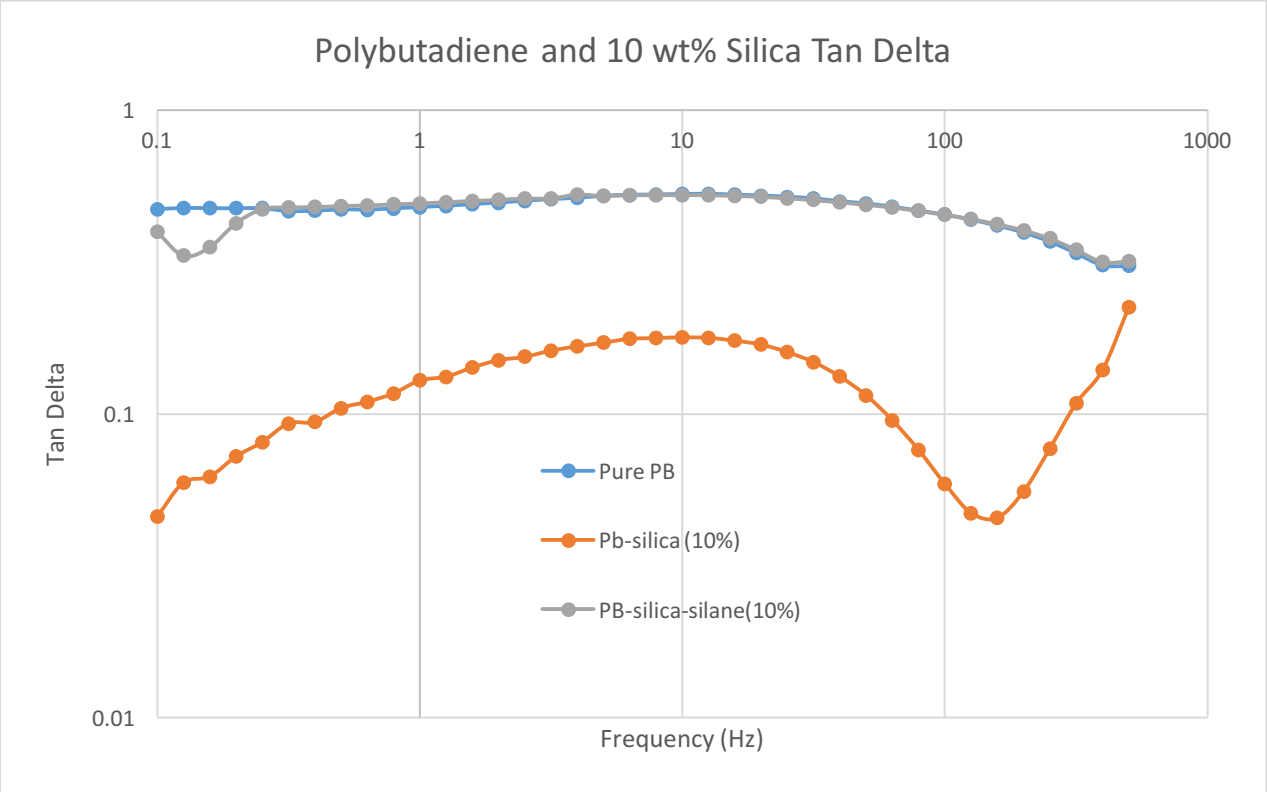

Figure 47: Tan delta versus frequency for polybutadiene and 10 wt% silica

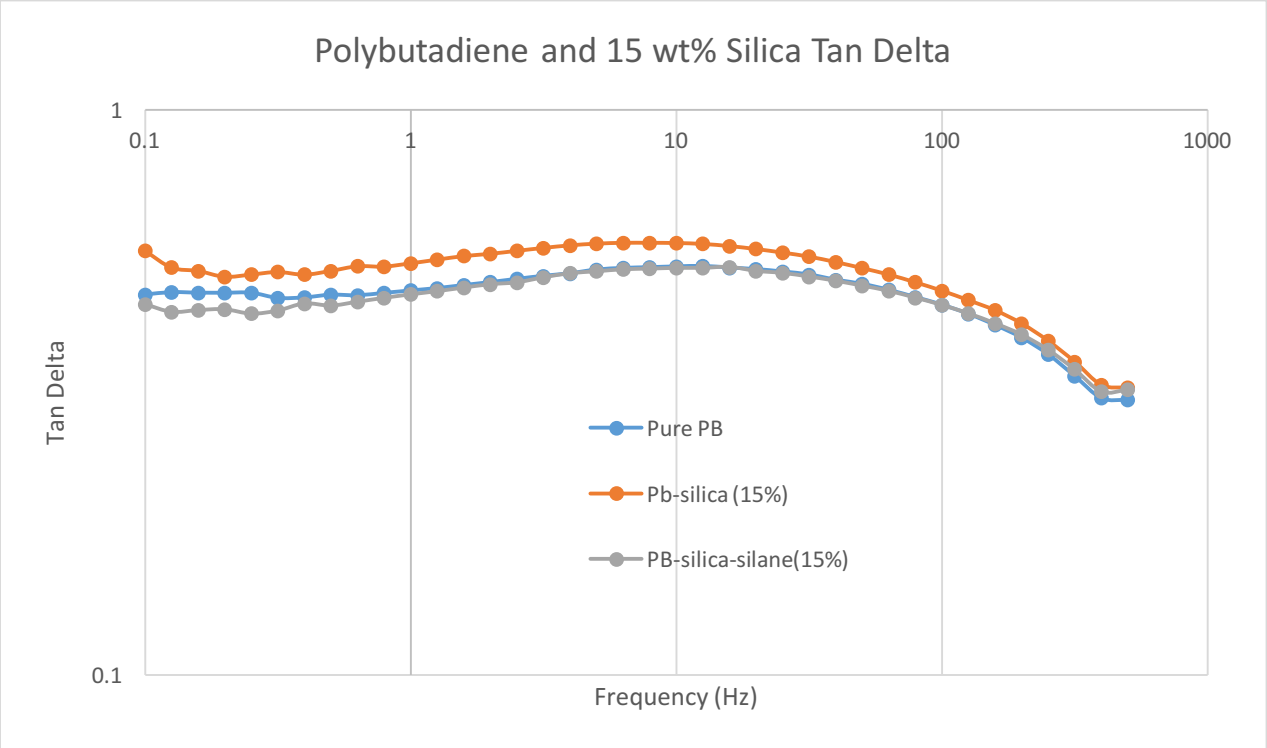

Figure 48: Tan delta versus frequency for polybutadiene and 15 wt% silica

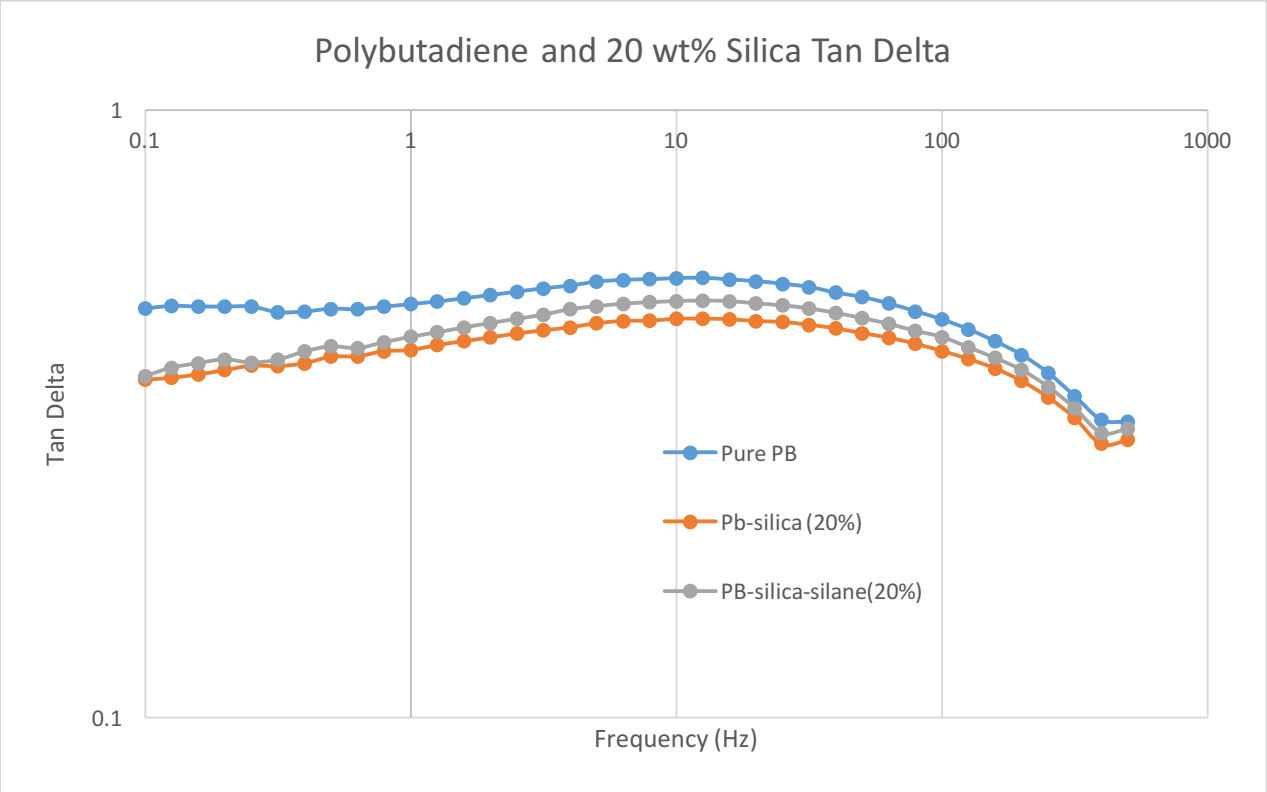

Figure 49: Tan delta versus frequency for polybutadiene and 20 wt% silica